VOL. XXV 1914

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

LIBRARY
Brigham Young University

COLLECTION ON GEOLOGY AND ENGINEERING

FROM DR. ALBERT CLARENCE BOYLE, JR.

CALL NO. V. 25

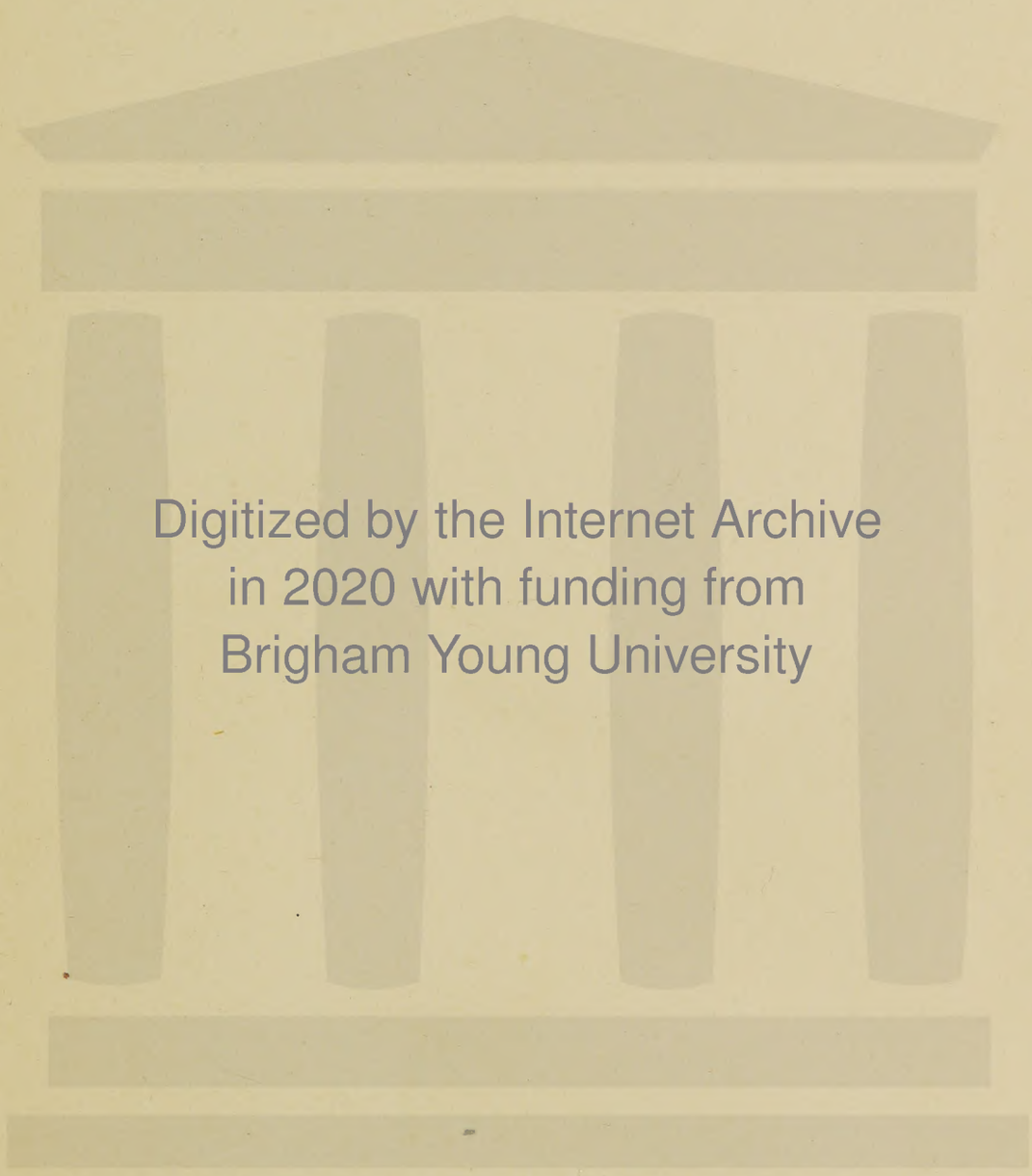
ACC. NO. 157563

UNIVERSITY OF UTAH
LIBRARY

CLASS BOOK

THE GIFT OF

PERIODICAL

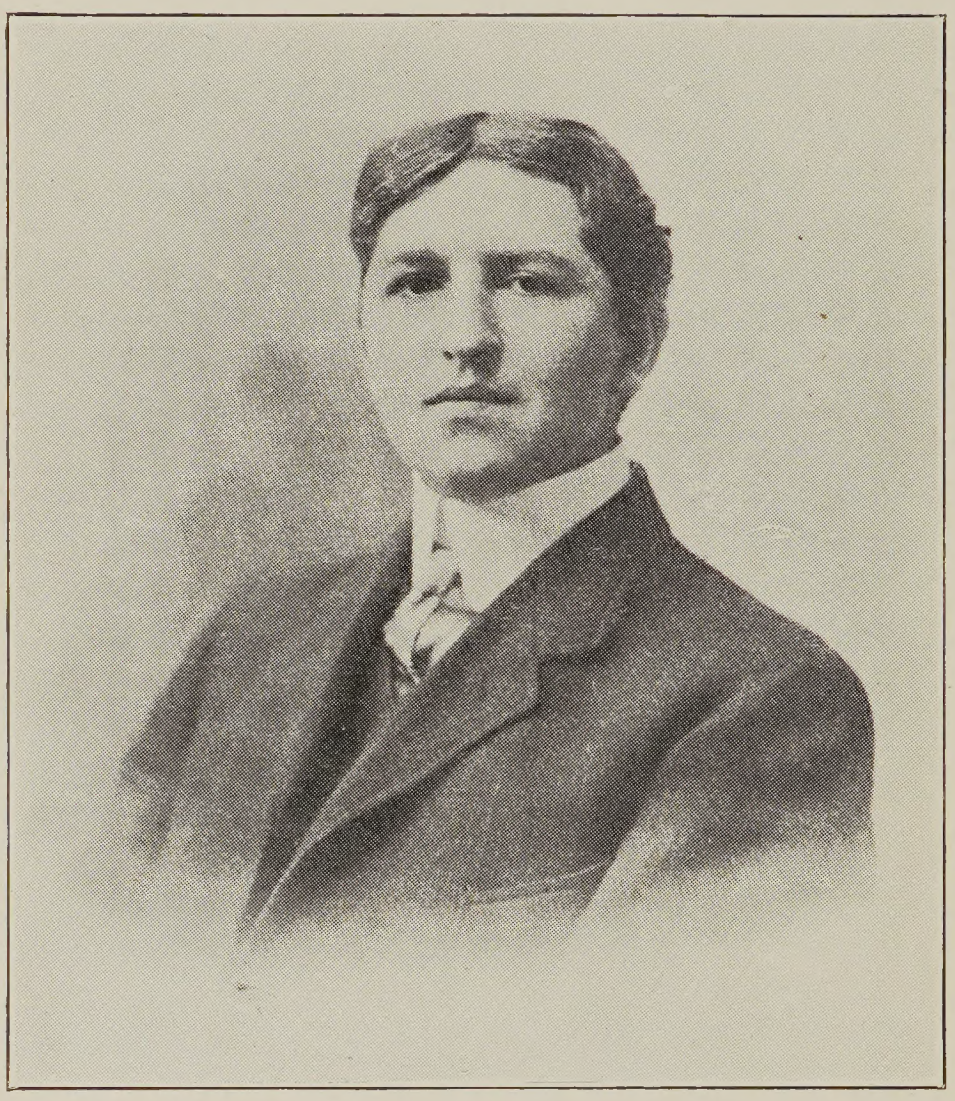


Digitized by the Internet Archive
in 2020 with funding from
Brigham Young University

https://archive.org/details/transactionsofam25phil

UNIVERSITY OF ILLINOIS LIBRARY

UNIVERSITY OF ILLINOIS LIBRARY



J. Austin Fidlam

TP
250
.E542

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XXV

157563

TWENTY-FIFTH GENERAL MEETING

NEW YORK CITY, APRIL 16, 17, 18, 1914

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

1914

Copyright 1914, by the American Electrochemical Society.

Permission to reprint parts of the *Transactions* is hereby granted to current periodicals, provided due credit is given.

This Society is not responsible for the statetments and opinions advanced in papers or in discussion thereon.

One copy of each volume of the *Transactions* is supplied gratis to each member of the Society in good standing.

Prices of Volumes I to XXIV (excepting Vols. I, II and III), to non-members $3.00 per copy, to members (extra copies) $2.50, to public libraries, colleges, scientific societies and journals, $2.00. Volumes I, II and III, double above prices. Prices are for volumes bound in cloth, and include delivery within the postal union.

Non-members may obtain complete sets at 25 percent discount on above prices; members may obtain the volumes necessary to complete their sets at 25 percent reduction on above prices; public libraries, etc., purchasing complete sets to date, are allowed 10 percent reduction from above prices.

WARE BROS. COMPANY, PRINTERS
1010 ARCH ST., PHILA.

OFFICERS OF THE SOCIETY

PRESIDENT

F. A. LIDBURY
Term Expires 1915

PAST-PRESIDENTS

W. LASH MILLER
Term Expires 1915

E. F. ROEBER
Term Expires 1916

VICE-PRESIDENTS

C. F. BURGESS
S. A. TUCKER
C. P. TOWNSEND
Term Expires 1915

CARL HERING
W. D. BANCROFT
WM. BRADY
Term Expires 1916

MANAGERS

LAWRENCE ADDICKS
L. E. SAUNDERS
L. KAHLENBERG
Term Expires 1915

F. A. J. FITZ GERALD
J. W. BROWN
C. G. SCHLUEDERBERG
Term Expires 1916

H. C. PARMELEE
W. R. WHITNEY
C. G. FINK
Term Expires 1917

TREASURER

PEDRO G. SALOM
Term Expires 1915

SECRETARY

JOS. W. RICHARDS, Lehigh University, South Bethlehem, Pa.
Term Expires 1915

COMMITTEES

Executive Committee

E. F. ROEBER, Chairman
JOS. W. RICHARDS, Secretary
F. A. LIDBURY
W. D. BANCROFT
C. G. FINK
S. A. TUCKER
W. R. WHITNEY

Publication Committee

F. A. J. FITZGERALD, Chairman
W. D. BANCROFT
W. BRADY
E. F. ROEBER
W. LASH MILLER
F. A. LIDBURY, *Ex-Officio*
J. W. RICHARDS, *Ex-Officio*

99170

LOCAL SECTIONS OF THE SOCIETY

Wisconsin Section (Madison, Wis.)

PROF. C. F. BURGESS, Chairman, University of Wisconsin
DR. O. P. WATTS, Secreary, University of Wisconsin

Philadelphia Section

DR. CARL HERING, Chairman
S. S. SADTLER, Secretary, 39 S. 10th Street, Philadelphia

New York Section

C. G. FINK, Chairman, Chrome, N. J.
H. B. COHO, Secretary-Treasurer, New York City

Chicago Section

L. L. SUMMERS, Chairman, Chicago, Ill.
A. B. MARVIN, Secretary, Marquette Building, Chicago

Pennsylvania State College Section

C. A. WALTER, Chairman, State College, Pa.
P. E. KERN, Secretary, State College, Pa.

Pittsburgh Section

C. G. SCHLUEDERBERG, Chairman, Pittsburgh, Pa.
W. W. CLARK, Secretary-Treasurer, Bridgeville, Pa.

MEMBERSHIP COMMITTEE

LAWRENCE ADDICKS, Chairman, Douglas, Ariz.

L. H. BAEKELAND, Yonkers, N. Y.
C. W. BENNETT, Ithaca, N. Y.
C. F. BURGESS, Madison, Wis.
G. H. CLEVENGER, Palo Alto, Cal.
W. R. CLYMER, Cleveland, Ohio.
H. B. COHO, New York City.
E. L. CROSBY, Detroit, Mich.
J. B. DU FAUR, Queensland, Australia.
J. FORSSELL, Stockholm, Sweden.
F. C. FRARY, Minneapolis, Minn.
P. A. GUYE, Geneva, Switzerland.
F. HABER, Baden, Germany.
C. A. HANSEN, Schenectady, N. Y.
CARL HERING, Philadelphia, Pa.
A. T. HINCKLEY, Niagara Falls, N. Y.
A. HIORTH, Christiana, Norway.
W. R. INGALLS, New York City.
T. C. IRVING, JR., Toronto, Canada.
HAROLD JONES, Minas Geraes, Brazil.
C. A. KELLER, Paris, France.
K. KISHI, Tokyo, Japan.
C. F. LINDSAY, Bridgeport, Conn.
H. C. PARMELEE, Denver, Colo.
C. G. SCHLUEDERBERG, Pittsburgh, Pa.
E. P. SCHOCH, Austin, Texas.
A. STANSFIELD, Montreal, Canada.
GEO. C. STONE, New York City.
BRADLEY STOUGHTON, New York City.
L. L. SUMMERS, Chicago, Ill.
B. F. THOMAS, Chattanooga, Tenn.
R. THRELFALL, Birmingham, England.
C. P. TOWNSEND, Washington, D. C.
W. H. WALKER, Boston, Mass.
C. A. WALTER, Perth Amboy, N. J.

ADVERTISING COMMITTEE

G. A. ROUSH, Chairman, South Bethlehem, Pa.

TABLE OF CONTENTS

PAGE

Portrait of F. Austin Lidbury.....Frontispiece
Proceedings of the Twenty-fifth General Meeting..... 1
Annual Report of the Board of Directors..... 4
Annual Report of the Secretary..... 6
Annual Report of the Treasurer..... 9
Minutes of the Meeting of the Board of Directors..... 9
Members and Guests Registered at the Twenty-fifth Meeting..... 11
Members Elected and Qualified, September, 1913, to March, 1914..... 14

PAPERS.

Some Economic and Aesthetic Aspects of Electrochemistry—E. F. Roeber 17
Characteristics of Electrical Energy as Affecting Chemical Industries —C. P. Steinmetz 29
Notes on Power Transmission and Transmission Economics—P. W. Sothman 43
Some Economies in the Use of Energy in Electric Furnaces—F. A. J. FitzGerald 53
Power in Electric Furnace Work—W. S. Horry..... 59
The Power Problem in the Electrolytic Deposition of Metals—L. Addicks 65
The Power Problem in the Electrolytic Deposition of Metals—H. E. Longwell 73
Sources of Direct Current for Electrochemical Processes—F. D. Newbury 85
Electric Furnace Current Regulators—R. Turnbull..... 97
General Discussion on Power Problems in Electrochemistry.....107
Electrolytic Flames—W. D. Bancroft and H. B. Weiser.....121
Electric Steel Castings—C. A. Hansen.....133
Electric Furnaces for Steel Making—E. B. Clark.....139
Improvements in the Metallurgy of Zinc—G. C. Stone.....161
Electric Zinc Smelting—W. R. Ingalls.....169
Advantages of Southeastern Alaska for Hydro-Electrochemical Industries—W. P. Lass.....179
Leaching and Electrolytic Treatment of Copper Ores at Chuquicamata, Chile—E. A. C. Smith.....193
The Hydroelectric Treatment of Copper Ores—R. R. Goodrich.....207
Leaching of Copper Tailings—R. Gahl 243
Metal Inventory in an Electrolytic Copper Refinery—R. W. Deacon....255

PAGE

The Electrolytic Deposition of Zinc—J. W. Richards.....281
Addition Agents in the Deposition of Zinc from Zinc Sulphate Solution—O. P. Watts and A. C. Shape.....291
Electrodeposition of Cadmium, I—F. C. Mathers and H. M. Marble...297
Electrodeposition of Cadmium, II—F. C. Mathers and H. M. Marble..319
Electrodeposition of Nickel—C. W. Bennett, H. C. Kenny and R. P. Dugliss 335
Electrolytic Deposition of Brass on the Rotating Cathode—C. W. Bennett and A. W. Davison 347
A New Method for the Determination of Free Cyanide in Electroplating Solutions—G. E. F. Lundell.....369
Electrical Conduction at High Temperatures and Its Measurement—E. F. Northrup 373
Laboratory Notes on Some Electrical Properties of Silver Sulphide—F. A. J. FitzGerald 393
Polarization Single Potentials—C. N. Hitchcock.....415
New Cell Arrangement for Direct Determination of the "Free Energy"—R. Beutner 441
A Railway Track Cell—E. L. Marshall 467
Experiments on White Lead—R. S. Owens.....477
A Microscopic Study of Electrolytic Iron—O. W. Storey.....489
The Effect of Addition Agents in the Electrodeposition of Iron.—O. P. Watts and M. H. Li.....529
Index 537
Advertisements .....

VOLUME XXV. 1914.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWENTY-FIFTH GENERAL MEETING OF THE SOCIETY, HELD IN NEW YORK CITY, APRIL 16, 17 AND 18, 1914.

PROCEEDINGS OF WEDNESDAY, APRIL 15

Number of members registered, 157; number of guests registered, 167; total, 324.

The Publication Committee met at 7.30 P. M., and the Board of Directors at 8.30 P. M. at the Chemists Club. The annual report of the Secretary and Treasurer, and other actions there taken, aside from routine business, will be found immediately following in these proceedings.

PROCEEDINGS OF THURSDAY, APRIL 16

The annual business meeting of the Society was called to order at 9 A. M., in Rumford Hall, Chemists' Building, Dr. E. F. Roeber, president, in the chair.

The reading of the minutes of the Twenty-fourth General Meeting was dispensed with, the minutes being approved as printed in Volume XXIV of the Transactions.

The report of the Board of Directors, including those of the Secretary and Treasurer, was read by the Secretary, and accepted for publication in the proceedings of the meeting, to which it is appended. Briefly, this report shows a total membership of 1,376 at the close of 1913, a net gain of 26 during the year. The

financial report shows an excess of expenditures over receipts of $174.26, this deficit being caused by the expenses of the publication of the General Index. The net assets of the Society at the close of 1913 were: Cash on hand, $119.90; permanent investment, $6,121.11; total, $6,241.01.

The report was adopted as read.

In the absence of any of the Tellers of election, the report of annual election of officers was opened and read by the Secretary.

Report of the Tellers of Election.

To the American Electrochemical Society:

Gentlemen: Following is the count of the ballots cast in the election of officers for the year 1914-15:

For President: F. A. Lidbury 86, E. F. Smith 10, E. R. Taylor 8.

For Vice-President: C. Hering 75, W. D. Bancroft 73, Wm. Brady 55, E. G. Acheson 29, L. Addicks 27, L. D. Vorce 23, G. H. Clevenger 19.

For Managers: H. C. Parmelee 68, W. R. Whitney 56, C. G. Fink 48, L. H. Baekeland 45, F. C. Frary 42, Acheson Smith 23, T. F. Baily 12, C. P. Townsend 1, C. Baskerville 1.

For Treasurer: P. G. Salom 102.

For Secretary: J. W. Richards 104, G. A. Roush 1, W. R. Whitney 1.

Signed,

B. MacNutt,
S. S. Seyfert,
S. Fischer.

The Chairman then announced that, in accordance with the report of the Tellers, he declared elected the following:

President (for one year): F. A. Lidbury.

Vice-Presidents (for two years): Carl Hering, W. D. Bancroft, Wm. Brady.

Managers (for three years): H. C. Parmelee, W. R. Whitney, C. G. Fink.

Treasurer (for one year): P. G. Salom.

Secretary (for one year): J. W. Richards.

The Committee on Occupational Diseases in the Chemical Trades, appointed April 5, 1913, to co-operate with a similar committee of the American Chemical Society, reported no progress during the year, and asked to be discharged. On motion, the committee was discharged.

The business part of the session being concluded, the discussion of papers was taken up, and papers were presented by the following, and discussed as printed in these Transactions: P. W. Sothman, C. P. Steinmetz, F. A. J. FitzGerald, W. S. Horry, L. Addicks, H. E. Longwell, F. D. Newbury.

In the afternoon the meeting was called to order at 2 o'clock, and papers were presented by the following: W. D. Bancroft, C. A. Hansen, E. B. Clarke, G. C. Stone, W. R. Ingalls, W. P. Lass.

At 8 P. M. the President called the meeting to order in Rumford Hall, and delivered his Presidential Address. This was followed by a Smoker.

PROCEEDINGS OF FRIDAY, APRIL 17

The day was spent on a steamer excursion around New York Harbor, with visits of inspection at the plants of the American Smelting and Refining Company, the United Lead Company and the Waclark Wire Company, lunch being provided on board the steamer.

PROCEEDINGS OF SATURDAY, APRIL 18

The meeting was called to order at 9 A. M., in Earl Hall, Columbia University. By invitation a number of members of the American Electro-platers' Society attended this session.

Papers were presented by the following: E. A. C. Smith, R. R. Goodrich, R. Gahl, R. W. Deacon, J. W. Richards, O. P. Watts and A. C. Shape, F. C. Mathers and H. M. Marble (two papers), C. W. Bennett, H. C. Kenny and R. P. Dugliss, C. W. Bennett and A. W. Davison, and G. E. F. Lundell.

The afternoon session was called to order at 2 P. M., in the Metallurgy Lecture Room of the School of Mines. Papers were presented by the following: E. F. Northrup, F. A. J. FitzGerald, C. N. Hitchcock, R. Beutner, E. L. Marshall, R. S. Owens, O. W. Storey, O. P. Watts and M. H. Li.

The Secretary presented the following resolutions, which were duly seconded and passed:

Mr. President and Gentlemen: I move a cordial vote of thanks to the American Smelting and Refining Company, United Lead Company and Waclark Wire Company for opening their plants to the Society and its guests; to the Chemists' Club and the authorities of Columbia University; to the New York Section of our Society and the Local Committee in charge of arrangements, and particularly the Ladies' Committee, for their hospitality and their unselfish devotion of time, effort and, perhaps, money, toward the success of the Twenty-fifth Meeting of our Society.

At 7 P. M. a subscription dinner was held in Rumford Hall, Chemists' Building, following by dancing.

ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and Treasurer for the year 1913, the former containing the detailed financial statement of receipts and expenditures.

The net increase in the number of members during the year 1913 was 26, the membership at the end of the year being 1,376; 31 members have been elected since the first of the year; there are 15 applications on file waiting action of the Board.

The financial status of the Society during 1913 remained satisfactory. It is true, the report shows a loss in assets of $174.26, but when account is taken of the fact that during the year the Society bore the extra expense of the publication of the general index, amounting to $857.40, this fact is satisfactorily explained. During the year the $500 that has been held for a number of years for the Ferro-Boron Prize was returned to the donors. This amounts to an increase of $500 in the permanent investment of the Society, leaving all the bonds, amounting to $6,121.11, the entire property of the Society.

The following are the more important actions taken by the Board of Directors during the past year.

On April 2d it was ordered that the Ferro-Boron Prize of $500

be returned to the Pacific Coast Borax Company, with interest since the close of the competition. The sum of $250 *in toto* was placed at the disposal of the committee for assisting research. It was moved that the Society co-operate with the International Electrical Congress in San Francisco, 1915.

On April 26th the following Committee on Units, Nomenclature and Notation was appointed to co-operate with either National or International Scientific or Engineering Societies: Carl Hering, Chairman; C. O. Mailloux, J. W. Richards, G. A. Hulett, F. A. Wolff, Fritz Haber, P. A. Guye, C. Marie, F. Giolitti, J. A. Leffler and Sir R. A. Hadfield.

On September 27th the following Committee was appointed to confer with the Director of the Bureau of Mines in regard to the activity of said Bureau in Electrochemical and Electrometallurgical matters: W. R. Whitney, chairman; L. Addicks, William Brady, C. F. Burgess, G. H. Clevenger, F. A. J. FitzGerald, F. A. Lidbury and J. W. Richards. On petition of H. C. Parmelee, of Denver; J. B. Ekeley, of Boulder, and H. J. Wolf, of Golden, the Board authorized the formation of the Colorado Section of the Society, to include all members of the Society residing in the State of Colorado.

On October 24th the following sectional committees were appointed to foster interest in the work of this Society in their respective fields:

Experimental and Theoretical Electrochemistry: Irving Langmuir, chairman; H. M. Goodwin, L. Kahlenberg.

Industrial Electrochemistry: W. R. Whitney, chairman; C. G. Fink, F. Zimmermann.

Primary and Secondary Batteries: J. W. Brown, chairman; O. W. Brown, C. Hambuechen.

Electrochemical Analysis: W. T. Taggart, chairman; G. A. Hulett, E. P. Schoch.

Electroplating: G. B. Hogaboom, chairman; F. C. Frary, F. C. Mathers.

Electrolytic Metal Refining: L. Addicks, chairman; E. F. Kern, M. deK. Thompson.

Electrolytic Furnaces: S. A. Tucker, chairman; H. R. Carveth, A. Hirsch.

Chlorin and Caustic: A. H. Hooker, chairman; L. D. Vorce, W. H. Walker.

Fixation of Nitrogen: H. R. Moody, chairman; W. S. Landis, G. W. Morden.

Electric Furnaces: C. A. Hansen, chairman; G. H. Clamer, F. J. Tone.

Electrometallurgy of Iron and Steel: D. A. Lyon, chairman; R. Amberg, A. E. Greene, J. A. Mathews.

Ferro-Alloys: F. M. Becket, chairman; E. A. Beck, R. M. Keeney.

Electrometallurgy of Other Metals: H. C. Parmelee, chairman; R. Gahl, W. McA. Johnson.

SECRETARY'S ANNUAL REPORT.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: In 1913 the Society held two general meetings, one at Atlantic City, New Jersey, April 3d, 4th and 5th, at which the attendance was 84 members and 53 guests, total 143; the second at Denver, Colorado, September 9th, 10th and 11th, at which the attendance was 52 members and 59 guests, total 111. The Transactions of the Spring meeting include 14 papers, and those of the Fall meeting 18 papers.

In 1913 there were issued and distributed to our members two volumes of the Transactions: Volume XXII, the Transactions of the meeting held in New York City, September 7, 9 and 10, 1912, in joint session with the Eighth International Congress of Applied Chemistry; Volume XXIII, of the Atlantic City meeting, April 3, 4 and 5, 1913. These volumes contained 515 and 432 pages respectively.

The Transactions of the Denver meeting on September 9, 10 and 11, 1913, were issued February 17, 1914, and contained 396 pages.

The edition of each of the 1913 volumes was 1500 copies bound in cloth for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies bound in paper for distribution to the Faraday Society; 500 copies sewed, ready for binding, to be kept in stock.

Complete sets of the Transactions are still on hand, but the stock is rapidly diminishing, and Volumes I, II and III will

hereafter be sold at double price, according to action of the Board of Directors.

The stock of Volumes on hand December 31, 1913, was as follows:

Volume.	Bound in Cloth.	Bound in Paper or Stitched Ready for Binding	Total.
I	169	13	182
II	196	0	196
III	103	0	103
IV	131	234	365
V	82	234	316
VI	98	239	337
VII	99	247	346
VIII	115	248	363
IX	115	275	390
X	123	257	380
XI	117	261	378
XII	119	266	385
XIII	135	219	354
XIV	245	253	498
XV	237	222	459
XVI	7	522	529
XVII	175	518	693
XVIII	189	519	708
XIX	60	533	593
XX	59	535	594
XXI	62	554	616
XXII	74	548	622
XXIII	111	545	656

Condition of the Society in regard to Membership in 1913:

Members January 1, 1913		1,350
Elected and qualified as members in 1913		94
		1,444
Resignations in 1913	30	
Deaths in 1913	4	
Dropped for non-payment of dues	34	
	—	68
Members December 31, 1913		1,376

Financial Statement.

January 1, 1913, to December 31, 1913.

RECEIPTS.

Entrance fees		$ 470 00
Current dues		7,470 43
Sales of publications		895 51
Advertisements		484 38
Membership certificates		5 00
Sale of society pins		70 00
Interest on investments and bank account		319 07
Loans		2,000 00
		$11,714 39

EXPENDITURES.

Office printing		$ 445 19
Postage and express		1,182 00
Publications		5,293 54
Secretarial appropriation		1,281 28
Office expenses		308 57
Appropriations to local sections		125 00
Storage		84 00
Expenses of meetings		528 71
Faraday transactions, payment for extra copies		343 06
Commission on advertisements		49 00
Assisted research award		50 00
Engrossing membership certificates		2 40
Appropriation for symposium		4 90
Society pins		117 00
Return of Borax prize, with interest		550 00
Payment of loans, with interest		2,024 00
		$12,388 65
Excess, expenditures above receipts		$ 674 26
Permanent investment	$500 00	
Loss in cash balance	674 26	
Loss in assets		174 26

ASSETS, JANUARY 1, 1913.

Cash balance, January 1, 1913, on deposit		744 16
Cash box		50 00
Bonds held by the Society (cost price)	$6,121 11	
Ferro-Boron prize, held in trust	500 00	
Equity of Society in above bonds		5,621 11
		$ 6,415 27

ASSETS, DECEMBER 31, 1913.

Cash balance, December 31, 1913, on deposit	$ 69 90
Cash box	50 00
Bonds held by Society (cost price)	6,121 11
	$ 6,241 01
Loss in assets	$ 174 26

This deficit was caused by the expenditure of $857.40 for the General Index. Without this unusual expenditure the surplus would have been even larger than usual, viz., $683.14 against $549.93 last year.

Jos. W. Richards, *Secretary.*

TREASURER'S ANNUAL REPORT.

FOR THE YEAR 1913.

Jan. 1.	Cash balance	$ 794 16	
Jan. 1 to Dec. 31.	Receipts as per statement attached	11,714 39	
	Total receipts	$12,508 39	
	Expenditures 1913 as per statement attached	12,388 65	
	Balance December 31, 1913		$ 119 90
Dec. 31.	Balance, Wilbur Trust Co.	$ 1,218 09	
	Less checks not in	1,200 00	
		$ 18 09	
	Bal., Commonwealth T. I. & T. Co. $2,200 81		
	Less checks not in, Nos. 584 to 587 2,149 00		
		51 81	
		$ 69 90	
	Balance in cash drawer	50 00	
			$ 119 90

P. G. SALOM, *Treasurer.*

We have examined the Society's safe deposit box, and find it contained six bonds of one thousand dollars each.

We have examined the above statement of account and receipts and expenditures for the year 1913, and find the same to be correct.

CARL HERING,
S. S. SADTLER,
Auditors.

MINUTES OF THE MEETING OF THE BOARD OF DIRECTORS.

The meeting was held in the Chemists' Club, April 15, 1914, at 8.30 P. M.

Present in person: Roeber (presiding), Lidbury, Baekeland, Tucker, Bancroft, Hering, FitzGerald, Schluederberg, Addicks, Salom, Richards.

Present by proxy: Whitney, Miller, Taylor, Burgess, Townsend, Saunders and Kahlenberg.

Moved and carried that the Secretarial appropriation for a period of one year be fixed at $125 per month, as at present.

Moved and carried that the President appoint a committee to investigate the question of the incorporation of the Society, said committee being empowered to obtain legal advice if found necessary, and formulate a plan of incorporation if they found it advisable. The President appointed the Treasurer and the Secretary as such committee.

Moved and carried that the sum of $50 be appropriated for the current contribution of the Society to the Annual Tables of Physical and Chemical Constants.

Moved and carried that the Fall meeting of the Society be held in Niagara Falls, the first week in October.

Moved and carried that the Secretary investigate the feasibility of holding the Spring meeting of the Society in 1915 in the South—Chattanooga, Tenn., and Birmingham, Ala.—immediately preceding or following the meeting of the American Chemical Society in New Orleans, so that those attending might combine the two meetings.

The report of the Publication Committee was accepted and ordered filed. A letter was read by the Secretary from Mr. A. H. Cowles appealing to the Board of Directors against the rejection of a paper, written by him, by the Publication Committee. Mr. Cowles also appeared in person and explained his position to the Board of Directors. It was moved and carried that the Board of Directors, after hearing the Publication Committee and Mr. Cowles personally, sustain the action of the Publication Committee in rejecting Mr. Cowles' paper, because the Board believes the paper to be too obscure in its present form.

The Secretary was requested to compile a list of committees other than standing committees which have not been discharged.

It was moved and carried that before the next list of members is published, cards be sent to all members for the verification of their address.

Mr. Dorsey A. Lyon appeared before the Board and asked for the appointment of a committee to advise with the Director of the Bureau of Mines as to the nature of the Bureau of Mines' electrochemical exhibit at the Panama-Pacific Exposition at San Francisco in 1915. Mr. Lyon's request was referred to the now-existing committee appointed to confer with the Bureau of Mines.

The Secretary made his annual report for the year 1913. The Treasurer made his annual report for the year 1913, duly audited. These reports will be printed in full in the Proceedings of the Twenty-fifth General Meeting in Volume XXV of the Transactions.

Adjourned.

Jos. W. Richards,
Secretary.

MEMBERS AND GUESTS REGISTERED AT THE TWENTY-FIFTH GENERAL MEETING.

Members.

P. O. Abbé
Lawrence Addicks
C. H. Aldrich
H. I. Allen
H. S. Amer
F. L. Antisell
W. C. Arsem
D. K. Bachofner
L. H. Baekeland
T. F. Baily
H. A. Baker
W. D. Bancroft
Chas. Baskerville
E. A. Beck
C. W. Bennett
R. Beutner
Wm. Bjorkstedt
W. F. Bleeker
Walker Bowman
A. A. Breneman
Oscar Brophy
D. B. Browne
D. H. Browne
J. K. Bryan
C. L. Bryden
A. S. Callen
H. R. Carveth
M. A. Cleaves
Jesse Coates
H. B. Coho
Edw. A. Colby
H. R. Connell
Wm. A. Cowan
A. H. Cowles
J. S. Crider
Ed. L. Crosby
W. J. Cummings
N. E. Dabolt
Chas. A. Doremus
J. V. Dorr
H. G. Dorsey
Boyd Dudley, Jr.
Arthur S. Dwight
W. Dyrssen
Carleton Ellis
O. A. EnHolm
E. F. Eurich
C. G. Fink
F. A. J. FitzGerald
Chas. B. Foley
O. R. Foster
K. G. Frank
M. W. Franklin
T. B. Freas
R. H. Gaines
A. F. Ganz
R. E. Gegenheimer
Jas. J. Gerety
A. E. Gibbs
H. W. Gillett
R. R. Goodrich
A. J. Guerber
K. S. Guiterman
F. J. Hambly
Carl Hambuechen
N. V. Hansell
C. A. Hansen
J. L. Harper
L. O. Hart
Carl Hering
Henry Hess
Alfred Herz
H. D. Hibbard
E. F. Hicks
A. T. Hinchley
Alcan Hirsch
G. B. Hogaboom
Wm. G. Horsch
G. A. Hulett
Ernest Humbert
Otis Hutchins
W. McA. Johnson
C. M. Joyce
Edw. Keller
H. W. Kellogg
Philo Kemery
E. F. Kern
John Langton
F. A. Lidbury
P. M. Lincoln
S. J. Lloyd
E. G. Love
D. A. Lyon
Wm. D. Mainwaring
F. W. Manger
A. B. Marvin
E. J. K. Mason
J. A. Mathews
F. Mauelen
A. S. McAllister
J. Y. McConnell
W. W. Merrill
Chas. Mindeleff
J. M. Muir
R. E. Myers
E. F. Northrup
G. Ornstein
H. C. Parmelee
Chas. L. Parsons
J. C. Pennie
N. Petinot
Wm. B. Price
Jos. W. Richards
Chas. D. Robb
E. F. Roeber
G. A. Roush
Louis Ruhl
P. G. Salom
L. E. Saunders
W. M. Saunders
C. G. Schleuderberg
F. F. Schuetz
J. A. Seede
P. Sievering
S. Skowronski
Dyer Smith

Members (Continued).

E. A. C. Smith
W. O. Snelling
J. L. K. Snyder
E. G. Spilsbury
F. A. Stamps
Chas. P. Steinmetz
G. C. Stone
Bradley Stoughton
Ernest Stutz
W. T. Taggart
J. Takamine
J. B. Taylor
F. J. Tone
S. A. Tucker
R. Turnbull
L. C. Turnock
I. R. Valentine
G. D. vanArsdale
A. Van Winkle
C. H. Vom Baur
Alois von Isakovics
L. D. Vorce
A. L. Walker
C. A. Weeks
E. Weintraub
R. H. White
E. H. Whitlock
W. R. Whitney
A. M. Williamson
W. J. Wooldridge
Michael Yatsevitch

Guests.

R. J. Alexander, New York.
F. Andrews, Perth Amboy, N. J.
Mrs. W. C. Arsem, Schenectady, N. Y.
Mrs. L. H. Baekeland, Yonkers, N. Y.
R. L. Baldwin, New York City.
H. P. Banks, New York City.
A. Barnett, New York City.
Mrs. Chas. Baskerville, New York City.
Chas. B. Beck, Philadelphia.
E. H. Bedell, New York City.
V. A. Belcher, New York City.
D. D. Berolzheimer, New York City.
R. S. Bicknell, New York City.
Arthur Blaicher, Newark, N. J.
Mrs. A. E. Brisben, Port Richmond, N. Y.
Mrs. W. E. Brisben, Port Richmond, N. Y.
Mr. Brosell, Perth Amboy, N. J.
Chas. O. Brown, Pittsburgh, Pa.
H. E. Brown, Kingston, N. Y.
M. H. Burnett, Waterbury, Conn.
F. A. Buttrick, New York.
D. G. Campbell, New York City.
H. G. Cannon, Keokuk, Iowa.
H. Carmichael, Boston, Mass.
R. F. Clark, Jersey City, N. J.
C. C. Coates, New York.
Mrs. H. B. Coho, Mt. Vernon, N. Y.
Daniel S. Collins, New York City.
W. W. Colquhom, Zambridge Wells, England.
E. F. Cone, New York City.
Miss Kathleen Condon, New York City.
Mrs. Wm. A. Cowan, Brooklyn, N. Y.
Mrs. A. H. Cowles, Sewaren, N. J.
T. E. Crossman, New York City.
H. M. Cushing, Buffalo, N. Y.
Homer Darlington, Philadelphia.
A. W. Davison, Ithaca, N. Y.
Harry de Joannis, Bridgeport, Conn.
J. Deremoald, Perth Amboy, N. J.
Wm. H. Doering, Philadelphia.
Mrs. G. D. Dorsey, New York City.
L. C. Drefahl, Cleveland, Ohio.
Robt. P. Duglass, New York City.
G. W. Emanuel, Perth Amboy, N. J.
Marion Eppley, New York City.
G. H. Evans, Baltimore, Md.
C. D. Ferguson, Brooklyn, N. Y.
Wm. Ferguson, Brooklyn, N. Y.
Mrs. C. G. Fink, East Orange, N. J.
C. M. FitzGerald, New York, N. Y.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.

Guests (Continued).

L. W. Foss, State College, Pa.
Mrs. C. B. Foley, Dayton, Ohio.
H. E. French, Farmington, Conn.
Wm. T. Fuerst, New York City.
M. A. Gunck, S. Orange, N. J.
John Haddow, State College, Pa.
R. L. Hallett, Brooklyn, N. Y.
Wm. J. Hammer, New York.
Albert Handel, New York City.
H. M. Harbach, State College, Pa.
J. B. Herreshoff, Richmond Hill, N. Y.
J. B. Herreshoff, Jr., New York City.
Henry L. Hess, Jr., Philadelphia.
R. C. Hull, New York.
W. Hummell, High Bridge, N. J.
L. D. Huntoon, New York City.
Mrs. Otis Hutchins, Niagara Falls, N. Y.
W. O. Hutchins, Keene, N. H.
R. M. Hutchinson, State College, Pa.
E. B. Jewett, Clarksburg, W. Va.
J. E. Johnson, Jr., New York.
Mrs. C. M. Joyce, New York.
Mrs. H. W. Kellogg, Niagara Falls, N. Y.
Ernest Klepotko, New York City.
L. J. Krom, New York City.
Y. C. Kuang, New York City.
Walter Laib, Ritmann, Ohio.
M. J. Langdon, New York City.
F. C. Langenberg, Cambridge, Mass.
D. M. Liddell, New York City.
C. F. Limpsay, Bridgeport, Conn.
R. L. Lloyd, New York City.
E. A. Lof, Schenectady, N. Y.
Arthur Lowenstein, Chicago, Ill.
Alexander Lowy, New York City.
F. W. Lowry, State College, Pa.
G. V. Luerssen, State College, Pa.
G. P. Lunt, Boston, Mass.
W. W. Macon, New York City.
E. L. Marshall, Fremont, Ohio.
Mrs. A. B. Marvin, New York City.
H. A. Mayer, Portland, Ore.
J. S. McClenahan, New York City.
K. W. McComas, Perth Amboy, N. J.
James H. McGraw, New York City.
Albert Meyer, Irvington, N. J.
Geo. P. Moore, Hartford, Conn.
Mrs. G. P. Moore, Hartford, Conn.
H. E. Morse, New York City.
P. I. Murrill, New York.
A. F. Nagle, Jr., New York.
Arthur T. Neist, New York City.
M. Nikune, New York City.
Mrs. E. F. Northrup, Princeton, N. J.
G. L. Oldright, New York City.
John Painter, Brooklyn, N. Y.
I. Paris, Boston, Mass.
K. B. Pennie, New York.
T. P. Pennington, New York.
Allen M. Perry, New York City.
W. L. Raup, Perth Amboy, N. J.
Thos. T. Read, New York City.
A. R. Reed, State College, Pa.
A. R. Rhoades, State College, Pa.
C. L. Robbins, Wilkes-Barre, Pa.
Mrs. C. L. Robbins, Wilkes-Barre, Pa.
Mrs. E. F. Roeber, East Orange, N. J.
Chas. Rohrbach, Newark, N. J.
Mrs. G. A. Roush, South Bethlehem, Pa.
O. H. Rucker, New York City.
C. B. Sadtler, Denver, Colo.
E. M. Sargeant, Niagara Falls, N. Y.
J. A. Schweizer, Brooklyn, N. Y.
Mrs. E. M. Sergeant, Niagara Falls, N. Y.
A. R. Shaw, New York City.
Alexander Smith, New York City.

Guests (Continued).

M. C. Smith, New York City.
Tracy Smith, Waterbury, Conn.
W. F. Smith, Philadelphia.
Mr. Snyder, Perth Amboy, N. J.
P. W. Sothman, New York City.
H. N. Spicer, New York City.
S. A. Staples, New York City.
Geo. E. Stein, New York City.
E. R. Steinhardt, New York.
Miss. L. D. Steinhardt, New York City.
Chas. A. Stiehle, Irvington, N. J.
Jos. Struthers, New York City.
E. R. Sutcliffe, Leigh, Lancashire, England.
A. C. Terrill, Glendale, Cal.
Mrs. A. C. Terrill, Glendale, Cal.
F. P. Thausbindl, New York.
E. N. Todd, Newark, N. J.
K. Usui, Tokio, Japan.
T. Usui, New York City.
R. H. Vail, New York City.
W. E. Volz, New York City.
Mrs. Alois von Isakovics, Monticello, N. Y.
Mrs. L. D. Vorce, Detroit, Mich.
C. M. Wales, New York City.
C. H. Wang, New York City.
J. H. Ward, New York City.
J. U. Weggerate, New York City.
H. B. Weiser, Ithaca, N. Y.
Mrs. J. R. Wettstein, Perth Amboy, N. J.
Thos. F. Wettstein, Perth Amboy, N. J.
M. C. Whitaker, New York City.
A. P. Williams, Waltham, Mass.
W. W. Winship, New York City.
H. C. Wirt, New York City.
W. A. Wong, New York City.
R. U. Wood, New York City.
S. E. Woodworth, New York City.
E. Wurgler, Perth Amboy, N. J.
S. A. Zerega, New York City.

MEMBERS ELECTED AND QUALIFIED.

September, 1913—March, 1914.

September 27, 1913.

Gilbert S. Whitham, Antofogasta, Chile.
I. Grageroff, Choisy, P. Q., Canada.
S. R. Hanger, Altoona, Pa.
Kiosuke Kaneko, Akita, Japan.
Ernest Kraus, Newark, N. J.
Sven C:Son Lindberg, Uddeholm, Sweden.

October 24, 1913.

Ralph R. Parish, Waterbury, Conn.
F. L. Clerc, Estes Park, Colo.
E. J. Ericson, St. Louis, Mo.
Hugh P. Tiemann, Pittsburgh, Pa.
Geo. O. Deshler, Bingham, Utah.

November 28, 1913.

Paul Pleiss, New York City.
Thos. F. V. Curran, New York City.
Raymond F. Bacon, Pittsburgh, Pa.
O. A. En Holm, New York City.
J. P. Davenport, Elizabeth, N. J.
John V. N. Dorr, Denver, Colo.
Boyd Dudley, Jr., State College, Pa.
M. H. Bennett, Oakdale, Conn.

December 26, 1913.

Ralph S. Wenner, Metaline Falls, Wash.
J. Brownlee Henderson, Brisbane, Queensland, Australia.
Chas. T. Bird, Alliance, Ohio.

Members Elected and Qualified (Continued).

Phil. Jacob Forchheimer, Nürnberg, Germany.
Claude N. Hitchcock, Madison, Wis.
Edwin S. Dewey, Newark, N. J.
E. Bruce Pratt, Cleveland, Ohio.

January 23, 1914.

Frank H. Ramsey, Pittsburgh, Pa.
N. K. B. Patch, Buffalo, N. Y.
Chas. V. Ferguson, Schenectady, N. Y.
Henry A. Wentworth, Auburndale, Mass.
Robt. R. Goodrich, New York City.
Waldemar Dyrssen, Bethlehem, Pa.
Bjorn Raeder, Neerpelt, Belgium.
Carleton Ellis, Montclair, N. J.
Frank P. Gilligan, Hartford, Conn.
Percy Wilcox Gumaer, Columbia, Mo.
Clarence E. Peterson, Schenectady, N. Y.

February 27, 1914.

O. Dony-Henault, Mons, Belgium.
Chas. W. Merrill, San Francisco, Cal.
Oscar Brophy, Philadelphia, Pa.
H. S. Lukens, Philadelphia, Pa.
Ralph E. Gegenheimer, Waltham, Mass.
S. H. Stupakoff, Pittsburgh, Pa.
Wm. C. Moore, Lakewood, Ohio.
R. L. Sessions, Latrobe, Pa.
Alfred Herz, Chicago, Ill.

March 27, 1914.

A. F. Nathan, New York City.
Wm. B. Price, Waterbury, Conn.
D. F. Comstock, Boston, Mass.
W. S. Wyman, Augusta, Maine.
R. B. Silverman, Butte, Mont.
N. K. Chaney, Lakewood, Ohio.
H. A. Guess, New York City.
Jin Tachihara, Kobe, Japan.

The Presidential Address delivered at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 15, 1914.

SOME ECONOMIC AND AESTHETIC ASPECTS OF ELECTROCHEMISTRY.

By E. F. Roeber.

There is beauty in electrochemistry. The late Ludwig Boltzmann once said that of all artists the mathematical physicist is nearest to the world's Creator in the simplicity, directness and economy of his methods. Boltzmann made this remark in appreciation of the work of Kirchhoff and Maxwell. But we can apply it with equal truth to the electronic theory of our own time, which in the simplicity of its fundamental conceptions and in the comprehensiveness of its outlook has all the elements of pure beauty. The intellect which builds the structure of the atoms of the different chemical elements out of a positive electric nucleus in association with varying numbers of negative electrons, and makes his atoms produce the desired result, is a true creator, and his model has beauty like the visible world around us.

But more beauty is hidden in electrochemistry than the mathematical beauty of electrochemical theory. The research electrochemist who works out a new process, whether it is the reduction of aluminium from its oxide, or the conversion of amorphous carbon into graphite, or the production of calcium carbide from lime and coke, or whatever else, proceeds exactly along the same methodical lines as the artist, whether he be sculptor or painter or poet. The artist must take nature as it is. But for his work he takes from nature only what his imagination tells him to be essential to the idea he has in mind. It is this selective copying of the essential from nature, and this restriction to nothing but the essential, that makes a work of art beautiful.

The method is exactly the same with the creative electrochemist. He cannot improve on nature's processes and methods. All he can do is to imitate or copy nature's processes and combine them to a certain end. But because his goal is a certain

product he can select the starting materials which are essential and use nothing else, and he can select those processes of production which are essential and combine them into the most direct way of production, and produce only what is wanted. Artificial graphite made in the electric furnace is superior to natural graphite, because nature does not set out to make pure graphite, and man can. This makes the economic value of artificial graphite, but it also makes the artificial graphite process in the bold directness of its execution a true work of art. Wherever a process is so designed as to reach its object in the directest way with greatest economy, it is beautiful in the eyes of those who understand its rationale, and this is broadly true, and not restricted to electrochemistry. But the trained engineer's or scientist's intellectual eye is needed to see this type of beauty.

The thoughts on some particular aspects of electrochemistry which I want to submit to you for reflection tonight are of a cognate nature. They refer to the part which electrochemistry plays in the changes now going on in modern civilization in economic and æsthetic valuations. Our age is called an age of unrest and revolution. Whether we are really so much more restless than our ancestors is open to discussion and hard to decide. But that the scientific and concomitant engineering advances of the last century have brought an entirely new phase (in the phase-rule sense) into the play of human reactions which make up the history of mankind is not open to question. That the effects of modern science and engineering go far beyond their spheres of immediate interest is undisputed. What then is the effect of electrochemistry on two fields apparently so remote as political economy and æsthetics?

To express the question concisely I borrow Friedrich Nietzsche's phrase of the revaluation of values. My subject is: How does electrochemistry bring about a revaluation of economic and æsthetic values? I have brought Nietzsche's name into this discussion for still another reason. Nietzsche's brilliant and, at first sight, extraordinarily daring attempt of a revaluation of ethical values for the sake of creating the "Uebermensch" is perhaps in the final analysis of its positive aspects nothing more than a robust reassertion of what was strong and healthy in the viewpoints and valuations of classic Greece and Rome, but has

been lost in the last nineteen centuries to an exaggerated weak sentimentality. Nietzsche wanted to make restitution of this lost strength and health from classic Greece to modern civilization and thus create a new ethics. Now, it would seem that the effect of science and engineering on æsthetics is acting at present in the same direction in emphasizing the necessity of a return to the æsthetic viewpoint of classic Greece, as embodied in Socrates' view of the kinship of beauty and utility. It is for this reason that before speaking of æsthetic aspects of electrochemistry it is necessary to take up its economic aspects.

How are economic values being created by industrial electrochemistry? For this discussion Prof. Karl Knies' old and well-known conception is very useful that economic value is of three kinds—place value, time value, and form value. If I may use the text-book illustration, ice in winter in the Maine woods has no economic value because there is no market for it there. Brought to New York, it gets place value, because there is a demand for it in New York. Stored and sold in summer time, it gets an additional economic value—time value. Nothing has been done to the ice itself by man. The place value has been created by transportation, the time value by storing, and, as we will see later, these two points are of importance for the production of economic values by electrochemistry.

But for the present let us consider the third kind of economic value—form value—that is, the value created by the work done by man on the materials of nature, comprising mechanical work as well as chemical changes. Any chemical reaction produces or annihilates form values, economically speaking. But what is the distinguishing characteristic feature of the form values produced by the electrochemical industries? Let us take a few typical examples.

By the electrolysis of a solution of common salt we get caustic soda and chlorine, and we work up the latter perhaps into bleaching powder. The excess of the value of the caustic soda and bleaching powder over that of common salt is the form value produced by this process. So it is in the production of calcium carbide from lime and coke, of nitric acid and nitrates from atmospheric air, and so on.

The fixation of atmospheric nitrogen, representing an extreme

case, is most instructive. The raw material is atmospheric air, which as such has no economic value at all, so that we might say that in the production of nitrate from air the economic efficiency becomes infinitely high. It sounds very well to speak of a process with an infinitely high economic efficiency, but, if we take the time to remember that exactly this process which is now worked with fair financial results in Norway turned out a commercial failure some ten years ago in Niagara Falls, it is evident that our consideration must have been in some way so one-sided as to be misleading.

Why was fixation of atmospheric nitrogen a failure at Niagara Falls, and why is it a success in Norway? Not primarily on account of the process, because the Bradley-Lovejoy process worked with about the same technical efficiency as the Birkeland-Eyde process, though the apparatus was considerably more complicated. No, the decisive element which caused failure at Niagara Falls and success in Norway is the cost of electric power, which is three to five times higher in Niagara Falls than in Norway. And this brings us right to the root of the whole matter.

In discussing the economic value of some electrochemical products we have so far in a one-sided way compared only the value of the starting materials and of the end products, but we have entirely neglected the fact that in these cases we have not only to do with materials as such, but rather with the storage of energy in materials. The form value of many products of electrochemical industries is essentially due to their high energy content. A large amount of chemical energy is stored in electrochemical products; it is latent under ordinary conditions, but it may be gotten out wherever and whenever necessity arises, and this fact makes them useful and economically valuable.

Let us carry this consideration a little further by making use of the conception that the energy of a given system may be considered as the product of two factors—the capacity factor and the intensity factor, to use the terms of Ostwald. The total amount of energy remains the same, however the two factors may be changed, if only their product remains the same. But for the engineering applications it makes an enormous difference whether we make the capacity factor small and the intensity factor large, or the former large and the latter small.

In case of a waterfall the amount of water passing over the fall in a certain time is the capacity factor; the height of the fall is the intensity factor. The engineering requirements of the development of a waterfall with little water and a high fall are very different from the case of a lot of water with a small fall, though the energy may be exactly the same in both cases.

In the case of electrical energy the current passing in a certain time, measured in coulombs, is the capacity factor; the pressure in volts is the intensity factor. For electric power transmission we make the intensity factor, the voltage, as large as possible, in order to decrease the transmission loss.

In the case of electrochemical products, the weight of the materials is the capacity factor; the specific energy stored in them per unit of weight is the intensity factor. If we make the latter high, if we store a lot of energy in a little matter, it will again be favorable in reducing the cost of transportation.

Now, the element of transportation brings us to the conception of the place value of electrochemical products. If their form value is due to their high energy content, their place value is due to the possibility of chemical power transmission by material transportation of electrochemical products. These products of the electrochemical industries which are characterized by a high specific energy content are the principal medium of chemical power transmission.

There are two points of chemical power transmission to be specially emphasized. One is that it is not bound to a fixed route. It requires no line wires. It makes use of the ordinary transportation facilities for materials—railways, ships, etc. This is important, as it opens fields for chemical power transmission where electrical power transmission fails. For instance, there are still very large areas in this country, Canada and elsewhere which are so little populated that it would not pay to erect an electric transmission system to provide electric current for lighting. Here acetylene lighting is of supreme importance. And acetylene lighting is a case of chemical power transmission. At Niagara Falls the electric furnace produces calcium carbide from lime and carbon, and chemical energy is thus stored in the carbide, which is transported with its energy to any place where acetylene is required for lighting.

If transportation creates place value, storage creates time value. The use of chemical energy after it has been transmitted is not bound to a certain time, and that is the second important feature of chemical power transmission. With electrical energy which cannot be stored as such it is necessary to use the transmitted energy at once or to provide special means for storing it. In this respect chemical power transmission differs essentially from electric power transmission and is superior to it. Chemical energy is in itself essentially stored latent energy, and is used, therefore, in connection with other systems of power transmission for storage purposes, as in the case of storage batteries for electric power systems. The time value of calcium carbide is due to the fact that we can store it and can produce the acetylene just in the moment when it is needed for lighting.

There is a long list of electrochemical products which may be considered from the viewpoint of chemical power transmission. In bleaching powder we transmit the possibility of producing a bleaching or a disinfecting liquid whenever and wherever it is needed. In the series of peroxides we transmit their readiness to give off an atom of oxygen when and where we want it, or the reaction caused by it.

As pretty and concrete an illustration of chemical power transmission as we may wish we have in Hans Goldschmidt's ingenious aluminothermic reaction. The heat of reaction of aluminium and oxygen in forming alumina is relatively very high per unit of weight of aluminium. This is just the reason why the economical reduction of aluminium from alumina did not succeed until electrolysis was resorted to. Now, the fundamental idea of the aluminothermic method is that we have in metallic aluminium a medium which gives us by combination with oxygen a large amount of energy wherever or whenever needed. In thermit, the mixture of aluminium and iron oxide, we transport essentially the capability of producing at any place and at any time highly superheated molten steel for welding rails, for making repairs, and so on.

Again, in the new and important Norwegian nitrate industry we have an example of what we may call international chemical power transmission, as the economical value of Norsk saltpeter depends on its easy transportation by ship to other countries.

Thus we have at the same time creation of economic values in Norway by building up a new and important industry and creation of economic values in other countries by using the Norsk saltpeter to further agriculture.

I have dwelt on the relation of electrochemistry to chemical power transmission at such length because so many electrochemical products can be considered from this viewpoint. But it would be wrong to think that the whole of electrochemistry can thus be viewed. There is quite a number of very important electrochemical products in which with no stretch of imagination I am able to detect the aspects of chemical power transmission. But in all cases the form value is high.

In the case of aluminium we have the aspect of chemical power transmission only in the aluminothermic reaction, which, though big in itself, uses only a small amount of the total output of aluminium. In cooking utensils, in line-wire construction and other applications it is simply the mechanical and electrical properties of aluminium which count and which give it a high form value.

In electrolytic copper refining, the oldest and certainly one of the biggest electrochemical industries, the increase of form value is remarkable. It is a double one. First, the gold and silver are recovered; second, the copper itself is considerably increased in form value, due to its greater purity and resulting higher electric conductivity.

All those products of electrochemical industries which have nothing to do with chemical power transmission have a high form value, and must have it, because otherwise it would not pay to use an electrochemical process, in view of the high cost of electrical power. Hence the well-known axiom that in all such applications the use of electrochemical processes should be restricted as much as possible to the finishing touches, that is, to the refining of a comparatively advanced product.

In addressing the American Electrochemical Society, I need hardly show at length how this creation of economic values by the electrochemical industries has affected and is affecting modern civilization in its various phases. What was waste before, and what was considered a nuisance, becomes valuable. When the early Colorado gold seekers discovered the tungsten ore in

Boulder County, they cursed it, as it was not what they wanted. From their cursed "heavy black sand," electrochemistry has given to civilization ferro-tungsten and the tungsten lamp. From culm, the waste material of the anthracite coal mines, Acheson has given to the world artificial graphite, with its immense applications. Then there are the grand electric-furnace industries of artificial abrasives in use in so many walks of life. And so I could go on through the list of electrochemical products, down to Cottrell's electrostatic process of recovering values from obnoxious smelter fumes. Only this, however, I should add that electrolytic copper refining, itself made possible by the dynamo, has paid back its debt to electrical engineering, and, by furnishing high-conductivity copper, has made modern electric power transmission possible. And, as we have seen, in chemical power transmission electrochemistry has brought into modern civilization an absolutely new element by which what is now waste power is being scattered all over the world to build up industries, to further agriculture with fertilizers, to light cities with acetylene, to aid public health with bleaching powder, and to affect civilization in general in its most heterogeneous aspects. That electrochemists as true creators are bringing about a revaluation of economic values there can be no doubt. But what has electrochemistry to do with æsthetics?

If beauty is perceived through our senses, the first question is: How has modern engineering affected our senses? And the answer is simply that modern engineering has given us artificial senses in addition to our natural senses. In the old days, when the few apparatus in physical and chemical laboratories were home-made affairs, it was said that experimental physicists and chemists should be able to see with their ears and hear by touch, smell with their tongues and measure temperatures with their eyes. Now modern engineering has given us instruments and apparatus which really represent new senses and which are available to a much more general public. And, what is more, our artificial senses can be repaired or replaced by new and better ones, and they give us permanent records.

I am not stretching the meaning of the term senses in speaking of instruments as artificial senses. To the electrical engineer the readings of the voltmeter and wattmeter are as real and

as true indications of the outside world as though he put his head out of the window to feel whence the wind blows. Pyrometers give us real, though much more exact, indications of temperature, as the touch by hand of a hot body or the trained eye of the furnace man. The photographic camera is a new artificial eye that preserves the record of what it sees. Successive photographs put together in a moving picture show enable us to crowd into a period of five minutes what may have happened in a year. We can see crystals form and plants grow. The electric oscillograph gives us a record that permits us to see at leisure transient phenomena that happen in portions of a second, and study over them for hours. The telephone extends the ability of the human ear so that it can hear in Denver what is said in New York. And if we hear our children of three or four years talk to us over the long-distance telephone in such a self-evident matter-of-fact way as though they were sitting on our knees, we cannot escape the conclusion that a new generation is rising to which the perception of the outside world comes through new senses and which consequently looks at the world with new eyes. What has electrochemistry to offer to this new generation in æsthetic ideals?

It seems to me that the fundamental contribution which electrochemistry has to make to æsthetics is to carry to its last consequence the principle that waste can never be beautiful. Of course, this principle is as old as art. Waste of words in a work of literature, waste of lines or colors in pictures, waste of space in architecture, have always been considered the opposite of beautiful. But the growing multiplicity of our sensual knowledge due to the magnified and projected extension of our senses forces us to see waste where our ancestors saw beauty and had a right to see beauty.

Permit me to concentrate my remarks on the one subject that is uppermost in this connection in the minds of American electrochemists—the question of the power development of Niagara Falls. I use it as a clear-cut example of what revaluation of æsthetic values by electrochemistry means. The magnificent group of electrochemical industries of Niagara Falls, which are the pride of every American electrochemist, and should be the pride of the whole American nation, suffers seriously from

the power famine due to the cessation of power development by international agreement between the United States and Canada. This agreement is based on the alleged will of the people of both countries to have the falls preserved as a scenic spectacle, on the principle of conservation of natural beauty. The battle cry is conservation of natural beauty for the people.

The counter-argument has been made that the natural beauty conservationists want to conserve something that no longer exists. With this I agree, but I hesitate to agree with the form usually given to this argument, namely, that if Niagara Falls could be preserved in its original magnificence it would be worth while, but that Niagara as a majestic spectacle has never belonged to the present generation, that its beauty had been given up to noisy and offensive exploitation long before the first power station was erected.

This may be true, but it seems to me that this argument does not reach the root of the matter. The beauty of Niagara Falls, like all beauty, is subjective in the onlooker. The question is, simply: What do we see when we stand at the brink of Niagara Falls?

Our ancestors, who knew nothing of the principle of conservation of energy, of transformation of different forms of energy into each other, looked simply at the material side of the falls and saw beauty and had a right to see beauty. And if we force ourselves into such a one-sided attitude of mind we can still see beauty.

But if we stand as modern men at the falls, with a free attitude of mind, we don't see simply water; we see power. We see the possibilities of using this power for electric power transmission for lighting, traction and industrial purposes on a wider area. We see the even greater possibility of storing this power in electrochemical products and utilizing them all over the land, in all walks of life. If we look at the falls with this attitude of mind, which is the natural one for us, every cubic foot of water that goes thundering over the falls unutilized appeals to us as waste and nothing but waste.

Now, waste can never be beautiful. If the artist's selection of the essential and nothing but the essential makes a work of art beautiful, anything that strikes our imagination as waste must

prevent æsthetic enjoyment. If we could look at Niagara Falls with the eyes of our ancestors it would be different, but in full possession of our extended senses, which an engineering age has given us, the Falls of Niagara—as much of them as is not utilized—must simply impress us as a waste of immense proportions.

And just the element of bigness, which was an element of beauty to our ancestors, has necessarily become to us the reverse, emphasizing only more emphatically the criminal negligence of letting waste on such a tremendous scale go on. Undeveloped Niagara Falls remains spectacular even to the modern man, but it is no longer beautiful.

The perverse mind of Nero could enjoy the spectacle of Rome burning. Children and fools might naively enjoy a conflagration that would consume for spectacular purposes a million tons of coal a week. We let the equivalent waste go on in water-power, and hear it called saving beauty for the people.

But there is little use in arguing in æsthetic matters. All we can really do is to make people see for themselves, use their own senses, all of them, their natural ones and their artificial ones. This is what the engineering developments tend to do every day, and we can rest assured that, as certainly as day follows night, a new generation is rising that will use its senses, all of them, and make its own æsthetics.

And when that time has come and people look at the Falls of Niagara running dry, their imagination will reveal to them immense beauty, health, wealth scattered by electrical and chemical means all over the country, while the grandeur of the whirlpool rapids, unchanged and undiminished, will have a higher æsthetic value, a deeper meaning of beauty than it can possibly have for us. The world will then smile at the æsthetic scruples of so many well-meaning people of our own time, and will wonder what all that talk of saving nature's beauty was about.

157563

A paper presented in the Symposium on Power Problems in Electrochemistry, at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914, President E. F. Roeber in the Chair.

CHARACTERISTICS OF ELECTRICAL ENERGY AS AFFECTING CHEMICAL INDUSTRIES.

By C. P. Steinmetz.

Industrial operations require materials, energy and labor. The characteristics of electrochemical operations, and chemical operations in general, are that very frequently the item of materials, and still more so the item of energy, predominates over that of labor. While, therefore, the economical supply of energy is important for most industries, it is especially so for the chemical industries. As a result, we see that where the product of the industry is relatively low in value, as in the steel industry, the industry clusters around nature's stores of energy and materials: where coal and ore are available. Electrochemical industries cluster around nature's store of hydraulic power: Niagara Falls and other large water-powers.

In the supply of energy we have to rely upon nature's stores, of which only two are sufficiently large to come into serious consideration, that is, the chemical energy of fuel, mostly coal, and the hydraulic energy of water-powers, made available by electrical transmission. This, in many cases, also carries the chemical energy of fuel to its place of consumption.

Considered merely as the raw material, as bulk of energy, the chemical energy of fuel is very much cheaper. The chemical energy of coal can be bought under favorable conditions near the mines at rates as low as 0.01 cent per kw. hour. The lowest values of electrical energy derived from water-powers, for twenty-four-hour-a-day service, three hundred and sixty-five days a year, in those favorable locations where the hydraulic development has been very simple and the supply is very cheap—as in some big water-powers in Norway, etc.—the values which may be reached there are about 0.1 cent per kw. hour, which means that, in general, the lowest cost of electrical energy from water-power

is about ten times that of the lowest cost of the chemical energy of fuel.

It means, then, that electrical energy can compete with the chemical energy of fuel only in those cases where compensating advantages occur. There are two such cases: first, where electrical energy can accomplish chemical results which cannot be accomplished by the chemical energy of fuel. Illustrative of these are aluminum reduction, carbide production and fixation of nitrogen; and, second, where the economic losses in transformation, the economic losses of making the chemical energy of fuel available by converting it to the form in which it is used, are such as to make the cost of the energy required by the industry when derived from the chemical energy of fuel higher than the electrical energy derived from hydraulic power. The most typical illustration of this, as we all realize, is the mechanical energy supply. While the chemical energy of fuel costs about one-tenth of what the electrical energy from water-power costs, when we convert the chemical energy of fuel into mechanical energy, by steam plant, with boilers, etc., and take into consideration the interest on the investment, the inefficiency of the thermo-dynamic energy transformation as a whole, from the chemical energy of fuel to the mechanical energy at the fly-wheel, we find that almost always the cost of the mechanical energy derived from chemical energy of fuel is higher than that when derived from the electrical energy transmitted from the water-power, other things being the same, that is, the same continuity of service.

Since electrical energy can come into consideration compared with the chemical energy of fuel only in those cases where the circumstances of its use make it economical and compensate for its original higher cost, you see that the utility of electrical energy depends on, and is determined by, the characteristics of this energy, and that brings us to the consideration of the characteristics of electrical energy which make is specially suitable for chemical industries, and, as we are gradually beginning to see, for all industrial uses.

The first characteristic which I wish to mention is the possibility of concentration to an almost unlimited energy density. This means that by electrical energy we can bring about chemical

actions which cannot be brought about by the relatively low energy density available by combustion from the chemical energy of fuel. So, in electric furnace processes, we can reach temperatures two or more times as high as the highest temperature possible by the combustion of fuel, even with hot blasts and all other auxiliaries. That means that chemical operations which cannot be carried out by fuel, as the reduction of calcium, for instance, either as metal, or, as is more commonly the case, in combination with carbon in the form of carbide, are not possible chemically in an economical way, because of the low intrinsic energy density of fuel, but are possible by electric energy. The reduction of aluminum cannot be brought about like that of iron by the chemical energy of fuel. It requires the higher concentration of electrical energy. The fixation of nitrogen can be brought about in the arc by its high temperature or by its internal electrical action. It cannot be brought about in an economic manner by the flame resulting from the chemical combustion of fuel.

In those fields, then, where a higher energy density is required, electrical energy stands without a rival, irrespective of the cost, and the economy of energy supply merely determines the utility of the product in the industry. It determines how far aluminum can compete with other metals which can be produced cheaper, or can be produced by reduction by fuel. It determines how far calcium carbide can be utilized in competition with illuminating gas, how far it can be worked up into cyanamide to compete with other fertilizers.

The second characteristic of electrical energy is its control. We can control electrical energy very much more closely than the chemical energy of fuel produced by chemical combustion. We can produce electrical energy without surrounding foreign materials which would enter as contamination. Therefore our electrical energy finds a usefulness in chemical or other industrial processes where a very close control of the energy is called for, and where the exclusion of contamination by foreign materials, which is practically unavoidable when you use fuel as the source of energy, is essential, because the inclusion of these contaminating foreign materials would be an economical disadvantage. So we see in copper refining, in many electrolytic and many smelt-

ing processes, as the production of high-grade tool steel, electrical energy has the advantage, not by its cheapness, but by the control of temperature and by the exclusion of contamination.

The dominating characteristic of electrical energy is that it can be transported or, as we usually call it, transmitted economically through practically unlimited distances and distributed commercially. In this respect it is not superior over the chemical energy of fuel, because coal also can be transported economically, and even to greater distances than electrical energy, but the predominating advantage of electrical energy is its economical efficiency of conversion to other forms of energy. This is really the dominating feature.

Where we want chemical energy or mechanical energy, we can convert the electrical energy derived from hydraulic power with very simple apparatus, at relatively low cost of installation, with efficiencies ranging high up in the nineties in percentage. But if you start with the chemical energy of coal and convert that into mechanical energy, or into some other form of chemical energy, we reach energy efficiencies averaging, probably, less than 10 percent. We have economic efficiencies still much lower, and considerable installation is necessary.

To illustrate, take the problem of producing mechanical energy from the hydraulic energy of water-power and from the chemical energy of fuel. For the hydraulic energy of water-power at the turbine, all that is required is an electric generator, a transmission line and a motor. These are relatively simple. Probably the total losses in generation and transmission and reconversion into mechanical power are 10 percent—not much more. Take the energy of coal. First, that item of transmission, in the transmission line, has also to be paid in the transportation of coal, but then the chemical energy of fuel is not available where you want it, in industry, in the form of mechanical motion; it means combustion in furnaces, means steam boilers and steam engines, and it means, finally, when you get the mechanical power, the power is in one big bulk, which, in many cases, will have to be once more reconverted to electrical power, distributed, and reconverted into mechanical power at the point where you want to use it.

So the result of this economic efficiency of conversion of elec-

trical power is that, starting initially with hydraulic power, at a cost ten times higher than that of the chemical energy of fuel, when we have finally transformed it into the form of power which is to be used, no matter what power it is, except heat, disorganized energy, we find the hydraulic power is the cheaper one. As we all realize, the energy derived from hydraulic power is produced at lower cost where big bulks are needed, as in chemical industries, than energy derived from coal.

There is, however, one characteristic of electrical energy which is a very serious disadvantage, and restricts its usefulness by the limitations imposed by it, and that is that electrical energy cannot be stored, but has to be consumed at the same rate at which it is produced from other forms of energy. There is the so-called storage battery, which stores energy by the converting of the electrical energy into chemical energy, and then reconverts it into electrical energy; but in the general energy supply we may dismiss this from the beginning as economically impossible. Comparing the chemical energy of coal with the electrical energy derived from hydraulic power: If the energy supply is interrupted for several months in the year by the stoppage of navigation, by the scarcity of water, and the coal supply going by boat is suspended, it is not a serious handicap when we use the chemical energy of fuel. It merely means, before the closing of navigation interrupts the coal supply, that a few hundred or a few thousand tons of coal must be stored up, and it is just the same whether we use one hundred tons of coal all at once, in a big furnace, or use it in such a way that it will last us for several months—the cost of energy per unit is the same. But we would not think of using the storage battery to store enough electrical energy in the spring flood to last over the dry season of the year when the river runs dry. Economy would not permit it. The storage battery is feasible only for small amounts of power where cost is of no consideration.

This means, then, that electrical energy must be consumed at the rate at which it is produced, and this makes the cost of electric energy dependent on the rate of its consumption in the same manner as the cost of energy is dependent on the rate of its production.

Now, this is well known, but not always realized when con-

sidering the industrial use of energy. We are rather inclined to figure that a chemical process requires so many kilowatt-hours of electricity per ton of product, but that does not yet determine the economy of the process. A modification of it, requiring 50 percent more energy, but permitting a rate of the use of the energy that would make it cost half, or less, would really be more economical *in toto*. So you see the energy item by itself, measured by kilowatt-hours, does not determine at all the economy of the industrial use of energy, but it is very largely influenced by the rate of use of the energy.

In the extreme case, which we do not need to consider here, outside the range of chemical industry, the cost—I mean *cost,* not *price*—of electrical energy generated in the same big power station, may vary in a range of more than 1 to 200; that is, power may be sold economically and profitably at one-half cent, or less, per kilowatt hour, while power generated at the few hours of the annual peak of the load would cost the station more than one dollar per kilowatt-hour—these are actual figures.

So you see how enormously the cost of electrical power may vary with the rate of its consumption. The cost of electric power consists of two parts—the fixed cost and the proportionate cost. Consider, as an illustration, a steam plant generating electric power. A part of the cost of operating the steam electric power plant, roughly about one-half, is the same, regardless whether the plant is running at full load, or turning out no electrical energy. It is the interest on the investment, depreciation, some of the maintenance repairs, even some of the labor items, as general management and supervision. That is the fixed cost. Then, there is the cost proportional to the power turned out, which is the largest part of the cost of fuel, oil, etc.

Now, suppose, instead of running this plant twenty-four hours a day for three hundred and sixty-five days in the year, where the cost of electrical energy will be lowest, we run it only twelve hours a day—half the time—you see the output of the station in energy is reduced to one-half. We sell the consumer only one-half as much energy, but the fixed cost of running the station is the same as before. The proportionate cost has been cut down to one-half—the total cost of running the station now is three-quarters what it was before, and, with only half the

energy output, it means that the cost of energy is 50 percent higher. To take an extreme case, if we turn out energy for one hour a day, running the station only one hour a day, the fixed costs being the same, the proportionate cost being reduced to 1/24, the total cost is 13/24, but we produce only 1/24 of the energy, and that means that the cost of the energy, for one hour a day use, is thirteen times higher than for twenty-four hour use.

In the case of a hydraulic station, we may say, as a rough approximation, that the proportionate cost is negligible compared to the fixed cost. That means it costs just as much, in a hydraulic station, whether you turn out any energy or not. If you can run twenty-four hours a day, three hundred and sixty-five days a year, you realize the least cost. If you run only one-third the time, the cost per unit, per kilowatt-hour, is three times higher. If you run only one hour a day, the energy cost is twenty-four times as much.

We see, therefore, that the economy of electric energy production depends on the continuity of producing it, twenty-four hours a day, three hundred and sixty-five days a year; and the cost of electrical energy is essentially determined by the ratio of the energy production by the station and the total energy which it could produce running twenty-four hours a day three hundred and sixty-five days a year. This is the ratio which constitutes the load factor of the station. The station load factor dominates the cost of electrical energy. A constant unity load factor, turning out as much electrical energy during the year as the station can produce, gives the lowest cost of electrical energy.

This, then, means that where the net cost of energy is essential, as in chemical industries, we must arrange the industry so as to operate continuously at a constant load. It is not sufficient to operate continuously twenty-four hours a day, three hundred and sixty-five days a year, but also at constant load, because, you see, if even momentarily, for a quarter of an hour, or a half hour, or one hour, you would require 50 percent more energy, that would mean you could, as an average, count on only two-thirds of the station output, as you have to provide for the possible excess.

That is the reason why the maximum demand of the user is such an essential element fixing the cost. The desirable thing

is continuity of use, and also a maximum demand, not exceeding the average demand—that means, in other words, that a unity load factor at the consumer's premises determines the least cost. If the maximum demand exceeds temporarily the average demand, that means that provision must be made for spare station capacity, means that the cost of manufacturing electrical energy has increased. In studying the chemical industry, in the development of chemical industrial operations, it is essential that this question of maximum demand shall be kept in view; the maximum demand must be carefully considered, and is rather an important problem in designing in the electrochemical industry, and arranging so that there never will be a demand exceeding appreciably, even temporarily, the average supply agreed upon.

If I require 10,000 kilowatts of power for a chemical industry, I can get that power at least cost per kilowatt-hour when I use it continuously by day and by night and where I never take from the station more than 10,000 kilowatts; that is a mere electrical problem, a limitation of power. In the electric furnace processes we can very often bring it about by reactance, by intentionally providing a sufficient reactance so that the power can never appreciably exceed the average.

Now, that is a feature which is not always recognized. In general, designers of electric furnace installations always try to get high power factor. Naturally, the supply station also desires high power factor. Eighty percent power factor means only 80 percent of the generator and line capacity is used and paid for, while the remaining 20 percent is used up by idle currents in the generator and lines which do not represent power and therefore derive no income. If I could get the power factor at the furnace higher than 90 percent, it would be possible, in the variations of furnace operation, to run occasionally higher and get a maximum demand much exceeding the average. But in using the energy at 80 percent power factor, down to dead short circuit in the furnace, the power can never rise to more than 2 percent, so you exclude any possibility of maximum demand exceeding appreciably the average, and you thereby get a far higher station load economy. If it is a disadvantage to have a power factor as low as 80 percent, you can always compensate for it by additional machinery at a cost very much less

than the increased cost of electrical energy, which would result from a maximum demand exceeding the average demand in case of an attempted high power factor of the furnace, by synchronous condensers shunting the system and giving power factor compensation.

The first approximation to the minimum cost of electrical energy, then, means unity load factor, continuous use at constant energy demand, twenty-four hours a day, three hundred and sixty-five days a year. However, this power often comes from a water-power, and most water-powers, most rivers, run dry for a month or two during the year. That means a steam reserve must be provided, so that you can take care of the power supply during the dry period of the river flow. That means an increase in the fixed cost.

If, therefore, you can arrange the chemical industry so as to be able to shut down for some weeks, even a few months in the year, during the time when the water-power fails, you can eliminate the necessity of a steam reserve, and thereby very materially reduce the cost of electric power production, and, therefore, the cost of power for your industry. I speak only of the cost of power, not of the price, because the price always depends on the electrical operating company from which the chemical industry derives the power, and these considerations here would require educational work not only among the electrochemists, but also among the electric operating engineers, who do not all yet realize that selling power at a very low price is more economical than having the water run over the dam. It would apply where the electrochemical industry developed the water-power. That means that an operation with a shut down, or a great reduction of the energy demand during the failure of the water power, is more economical than continuous operation throughout the year. Chemical industries require a very large amount of power, and it is merely a problem in accounting to figure out whether it is more economical where large amounts of energy are required, and where the labor item is relatively small, that is, where the amount of energy per man runs into the hundreds and thousands of kilowatts, to give all the employees a vacation of a month or two at full pay, and shut down the indus-

try, or to run during the dry period of the river, at the higher cost of energy required when a steam reserve must be supplied.

Often you can save more in reduced cost of energy, resulting from the elimination of the steam reserve, during nine or ten months of the year, than you lose by paying the salary and wages of your employees during the bad period of the year. That, naturally, is an economic question which you can calculate exactly. Other questions coming in are whether you *can* shut down, whether this would not interfere with the industry. Naturally, you cannot shut down many chemical processes, like the electric furnace processes, at any moment, suddenly, without serious loss; but in most cases, probably, it is possible to shut down once a year for a period of some weeks, where you have previous notice, and, naturally, where the river is gradually drying, it is not a sudden shut down, but a shut down which you know of weeks before and can provide for.

The next item in lowering the cost of electrical power is the possibility of sudden shut downs, varying from a fraction of a minute to hours, or even days, by failure of the transmission line. Where an industry can be located close to the water-power, as around Niagara Falls, that is practically of no consideration. Where the industry is at the end of a transmission line, to guard against sudden shut downs, in case of accident, probably very few in number during the year, means a steam reserve or duplicate transmission line, and means a material increase in the fixed cost. So you see, where an electrochemical industry could be operated so as not to be affected by a sudden shut down for a short time at infrequent intervals, and where, in addition, it could be shut down on previous notice for some weeks during the year, during the dry period, the cost of energy would be materially lower than with constant use at unity load factor throughout the entire year, due to the reduction of fixed cost. Continuous operation throughout the entire year, therefore, is not necessarily the most economical.

There are many uses of electrical energy which cannot be carried out continuously twenty-four hours a day. Take, for instance, the oldest, which was the most important one, but which now is only a moderate part of the total electric energy consumption—lighting. That, inherently, is limited to a short

period of the day, probably not averaging over two hours or three hours a day throughout the year. That means that electric energy production for lighting inherently has a very poor load factor, and, therefore, electric energy supplied for lighting is very much more expensive than electrical energy supplied for other purposes. Industrial use, distributing power in factories and mills, which is limited to eight or ten hours a day, has a load factor better than lighting, and when combined with lighting still further increases the load factor, by not overlapping; even then it represents a load factor which, in the ratio of the total energy turned out to the total energy which the station could turn out, is fairly low. The same applies to transportation work, trolley lines, etc.

So even in a unified energy supply, where all the power demands of a city or territory are supplied electrically from the same system, we still find that the load factor will rarely exceed 50 percent, because there is always in the daily load curve one big valley, from six to eight hours during the night. There is even a flatter valley of ten or twelve hours during the day until the lighting peak comes on. That means, if we can find a use for the energy which the station is capable of producing and supplying during the valleys in the daily load curve, six or eight hours during the night time when there is practically no load, or during these sixteen or twenty hours, night time and forenoon and afternoon, when the load is light, all that energy could be produced without any increase in the fixed cost to the rest of the station, and that would be energy supplied without fixed cost. If you come to consider the case of the hydraulic station, where the fixed cost is practically the entire cost, you see that this energy would have practically no cost.

This applies where the water supply is sufficient, and you do not store up the water during the night time and run it over the turbines in the daytime. This is done in many stations, where the hydraulic installation is made twice as large as the available water-power, and then the station runs twelve hours a day, during the daytime, and shuts down for twelve hours during the night time, while the water is being stored up in the overflow. But even then, you see, by making the station twice as large, you have practically doubled your fixed cost.

The cheapest electric power is that electric power which falls entirely into the valleys of the daily load curve of systems which have a power demand of poor load factor for power of high value, as lighting and industrial power.

Any industry, therefore, which could utilize intermittent power, that is, could utilize power from six to eight or eighteen hours a day, should be able to get power at a price very much lower than the low values of continuous service brought about by a water-power, provided, of course, that both sides, the electrochemical engineer as well as the station operating engineer, realize the situation and are willing not to charge fixed cost, where there is no additional fixed cost, but rather take that additional profit which can be made in selling power to chemical industries which cannot be sold for any other purpose.

That, naturally, is a possibility, and I mention it to illustrate that the mere energy item does not characterize the economy of electrochemical industries. The possibility of intermittent energy use would make energy available so much more cheaply that a very much increased energy demand might still be more economical than a continuous energy demand.

What I wish to bring out is that, in studying economy of electrochemical operation, it is not sufficient merely to consider electrical energy as a commodity, measured by the kilowatt-hour, and having a value of so much per kilowatt-hour, for the value may vary enormously. The most expensive electrical energy is that used intermittently, in intermissions chosen by the consumer, while the cheapest is that electrical energy used intermittently, where the intermissions are chosen by the producer. If you can use power intermittently, dropping into the valleys of the load curve, you should get it at the cheapest possible rate. But if you use it intermittently, and you choose the period for its use that happens to coincide with the peak of the load curve of the power station, that means the most expensive form of power, approaching that of lighting rates, which have averaged, probably, ten times the rate of power in bulk.

So you see, the problem of electrical energy supply to the electrochemical industries and industries in general is not a simple problem, and requires a careful study of the conditions under which the energy can be most economically produced for

the purpose. It also requires going into the development of the electrical industry, and into the development of the chemical industry, modifying the latter so as to adapt itself to the specific conditions of the cost of electric power as determined by the absence of electric storage. And by this relation between the cost of power to the consumer compared with the cost of power production, the matter is determined, and so it is really determined by the unity load factor on the station. That is what I wish to bring before you.

A paper presented in the Symposium on Power Problems in Electrochemistry, at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914, President E. F. Roeber in the Chair.

NOTES ON POWER TRANSMISSION AND TRANSMISSION ECONOMICS.

By P. W. Sothman.

INTRODUCTION.

This is an age in which we have become accustomed to utilize electricity in some manner in practically every walk in life. Not only is it employed to solve difficult problems in manufacturing, transportation and mining, but it has been trained to serve our domestic needs in the household and even to lighten the burdens of the agriculturist. It is not surprising, then, to find it a fit companion to labor hand in hand with the great science of chemistry, so aiding in the accomplishment of gigantic results for the benefit of mankind which a few years ago would have been deemed impossible.

Inspiring as are these things when viewed in the abstract, we are, nevertheless, aware that they have not come about of themselves, or, like Topsy, "just growed," but are the result of long years of experimentation and study by many different investigators, each having added his share to the general store of the world's experience. Nor can we for a moment believe that we have arrived at a point where no further or new applications of electricity are possible. Each day reveals to us wider possibilities in the art, and the electrochemical field is no less prolific in these new developments than the other branches of electrical science.

The uses of electricity have multiplied so rapidly during the past few years that it has come to be the concern of many of us at least to find means for supplying power in the form of electricity in large quantities and at such a price that it will be economically available for the uses in hand. Moreover, in many instances we can find power existing in the primitive form of waterfalls, coal and peat beds, or oil fields, the location of which

are not suited to power utilization on the site, and transmission becomes a necessity. Such problems as these are for the engineer to solve, who by so doing contributes his share towards benefiting the human race.

The writer will first take up the more important methods that are available for the generation of power, and then pass on to the subject of transmission, showing what is possible in this direction, discuss some of the more important structural features, and outline general power costs at different voltages, treating the subject more or less from the viewpoint of the electrochemical engineer.

POWER GENERATION.

The principal means for the generation of electrical energy are steam, waterfalls, gas producer plants and oil engines. It is not necessary to enter into a description of how any of these are employed in practice, for plants of each type are common, although the last two have not yet been used in connection with large installations to any extent. It is the writer's feeling that a great opportunity lies in this direction for the economical production of power, and that the time will shortly arrive when we shall see these competitors of steam and water power take a very prominent place in electrochemical work. To illustrate this, a table has been prepared showing broadly the initial costs of power plants of the different types, including buildings, and the cost of electricity per kilowatt hour on the busbars as so developed, including all overhead and maintenance charges.

Initial Cost per Horse Power of Capacity.

Hydro-Electric Plant	Steam Plant	Gas Producers	Diesel Plant
$125.00	$100.00	$100.00	$100.00

Power Cost per Kilowatt Hour.

Hydro-Electric Plant	Steam Plant	Gas Producers	Diesel Plant
3.6 mills	6.25 mills	4.95 mills	5.62 mills

These figures are based on a load factor of 60 percent, and include fixed charges of 11 percent on the hydro-electric and steam stations, and 12 percent on the gas producer and Diesel

plants. The influence of load factor on the cost of power is well understood, and it will be appreciated that the high load factors which are attainable in large electrochemical operations favor not only water-power plants, but also those operated by producer gas and oil, for the high efficiencies of the latter two are most marked when the load factor is good.

As a matter of interest a table is copied which was published a couple of years ago showing horse-power used per employee in a number of industries. In some lines, such as in the manufacture of tools and also cotton and woolen goods, the power used is slight, and the power cost is a comparatively small portion of the whole, hence the actual price paid per kilowatt hour for energy, whether high or low, does not influence to any great extent the cost of manufacture. On the other hand, in certain industries like paper and pulp mills, the horse-power used per employee is large, and the cost of power forms a large percentage of the total cost. Although no figures are shown on electrochemical processes, we know that power forms one of the chief items of expense of operation, and it is of great importance to have a source of power for electrochemical work which shall not only be cheap at the present time, but which will continue to be cheap for a reasonably long period of years, notwithstanding the encroachment of demands for power by other industries which can easily afford to pay a higher price for it.

Nature of Manufactures	No. of H. P. used per Employee
Tools and implements	0.678 H. P.
Cotton and woolen goods	0.759 "
Miscellaneous manufactures	2.35 "
Lumber and woodworking	6.76 "
Paper manufacture	13.33 "
Flour and feed	15.93 "
Pulp grinding and excelsior	23.00 "

TRANSMISSION OF ELECTRICAL POWER.

The art of power transmission over comparatively great distances has made remarkable strides within the very few years since the time it was first conceived to be a possibility. It was as recently as 1891 that the first attempts were made to transmit power at 10,000 volts. The results were sufficiently gratifying to warrant the attempt of transmissions at 20,000, 30,000 and

40,000 volts. In ten years' time the voltage had climbed to 50,000, and then on up to 60,000 and 70,000 volts. Before the end of the year 1909 we had seen lines at 110,000 volts in operation. Now the mark has been set at 145,000 volts, and there is no reason to doubt that it will climb still higher.

These voltages have been the result of the pressing demand for the delivery of power at increasing distances or in greater quantities at a minimum conductor cost. It is, therefore, quite natural that the operator of electrochemical works should inquire whether this marked development in transmission cannot be taken advantage of by himself, with the same satisfying results obviously obtained by his confreres in other lines.

Such an inquiry cannot be answered in a broad and general way, for it is only by a careful study of the conditions existing in each particular case that the information desired can be obtained, and the desire of the writer is to be of aid in such study by setting down the following considerations, which are in line with his personal experience.

The first question which comes to mind is: "How far is it possible to transmit energy electrically?" By this is meant the transmission of power in usable quantities, and not the dispatching of signals which can be sent by wire entirely around the earth or by wireless for a distance of several thousand miles.

The question is by necessity further limited to the consideration of how far power can be delivered commercially. Development in the electrical art has reached such a stage that it is not too much to say, from an engineering standpoint, that power in any amount may easily be transmitted on a straight-away line for a distance of at least 500 miles, and at that in a thoroughly reliable manner. By doing this, however, we might expect to obtain at the farther end of the line only 65 percent to 75 percent of the power fed into it, even with the use of liberal-sized conductors, because of the losses which inevitably occur, partly the familiar resistance or I^2R loss, and also to a great extent the so-called "corona" losses when the voltage is extremely high, as would be necessary with a transmission of this length.

At the present time there are no less than three long-distance lines in operation at approximately 145,000 volts, and the length of each is close to 240 miles. These are doubtless all well within

the present economical distance limit, which is dependent almost entirely upon the market for power and how much that market can afford to pay, it being assumed that the generating costs are not far from the average for plants of the class in question. Two of these systems are situated in the far West, where the cost of coal is high and where oil-produced power has as yet made but moderate headway; hence the state of the demand is such that it is possible to transmit power for this distance.

In districts where a cheap coal supply is available, such as in certain parts of the East, it is not profitable to transmit power to greater distances than about 175 miles, even when competing with steam, for if the power is required in such quantities as to warrant the construction of a substantial transmission line, it would also warrant the building of a modernly-equipped steam plant on the site of utilization which could supply energy at a cost as low as that of the transmitted power.

The use of a modern gas producer, burning coal costing $2.00 per ton, reduces the economical transmission distance of water-power costing to generate 4 mills per kilowatt hour to approximately 100 miles.

It may be mentioned that some of the longer transmission lines at present in operation are in reality a network, with sources of supply at several distributed points, which is a very favorable arrangement not only with regard to the cost of power, but also from an operating standpoint as well, for the crippling of a station or section of line will then only affect a few customers at most.

The next important consideration is that of voltage. As already mentioned, the reason for using high voltage is to keep the conductor cost as low as possible. With high voltage lines, however, there are other factors of expense which offset the saving in the size of conductors. For instance, wooden pole lines may be used for voltages up to 40,000 or 50,000, and upon them can be placed low-priced pin-type insulators. At 60,000 volts the almost universal practice is to employ steel towers, the cost of which, as a rule, is appreciably higher than the wooden poles. As the voltage further increases, very expensive pin-type insulators, or, what is more common, those of the suspension type, have to be used. With every step in the voltage which

involves a change in type of construction the line becomes more costly, so that the apparent saving in cost of conductors does not really apply.

At potentials above 100,000 volts the effects of corona become manifest. For ordinary purposes this phenomenon may be simply defined as the electric discharge which occurs due to the breaking down of the atmosphere in the immediate vicinity of the conductors when a certain critical voltage is reached. Such a discharge is accompanied by a loss of energy, and, when of any magnitude, is apparent in the dark as a glow or brush surrounding the cable. This critical voltage is dependent to a slight extent upon the temperature and barometric pressure (and hence altitude), and greatly upon the radius of the conductors, their distance apart and the condition of their surfaces. Moisture in the air, unless accompanied by fog or precipitation, has no effect.

The critical voltage at which corona starts becomes lower with smaller-sized conductors, and on this account alone it is not advisable to use at 110,000 volts a conductor smaller than No. 0 B. & S. gauge (8.25 mm.) cable, spaced 8 feet (2.4 m.) between centers, under ordinary conditions. At 130,000 volts and 10-foot (3 m.) spacings the size should be increased to at least No. 000 B. & S. gauge (10.4 mm.). It will readily be seen that the size of conductor necessary to avoid the formation of corona soon becomes too great, and thus the permissible voltage is limited. In this respect aluminum cables have an advantage over copper for transmission purposes, because of their lower conductivity, or, in other words, their size is greater than copper cables of equal conductivity, and, as their price on this basis is no greater, it is feasible to build lines of higher voltages with aluminum than with copper.

In the opinion of the writer, there should be no need of an intermediate voltage between 60,000 and 110,000 volts. If the conditions are such that a greater potential than 60,000 volts is required, it is worth while to adopt 110,000 volts, because the cost of construction of both lines and apparatus is not very much greater than for some intermediate voltage, and a considerable advantage is gained in the greater immunity of the higher voltage line from lightning troubles. The reason for this lies in the

fact that with line insulation sufficient for 110,000 volts a marked factor of safety with reference to the voltage of an ordinary lightning discharge has been attained. With lines at 150,000 volts there should be practically no trouble from lightning, with the exception of an occasional direct stroke on the line.

A subject which has recently received wide and renewed attention from transmission engineers is that of insulators. When the suspension-type insulator was brought out a few years ago it was believed that a means had been discovered which would make it possible to operate lines at any voltage that would ever be required. There is no doubt yet that this is so, but, instead of the complete solution having been reached at a bound, so to speak, it is now recognized that the matter was not such an easy one as was at first fondly hoped, but that the suspension insulator had to pass through a period of development, not necessarily yet at an end, especially in regard to its mechanical design, before it could satisfy all requirements.

Some insulators which have been placed on the market have given good satisfaction for a period of two or three years, and then the sections would begin to fail progressively. Examination has shown that this has been due mostly to cracks in the porcelain, brought about by the unequal temperature expansion of the different parts. To obviate this effect a modification in the design was necessary, and the results obtained by various investigators are such that troubles of this kind need not be experienced if sufficient care is exercised in the choice of design and in the testing of individual pieces. In addition to the improvement in the design of the insulator parts, it is possible, by the addition of protective end shields, to make the insulator as a whole very much more efficient.

The fact that the suspension insulators are flexible introduces several new considerations in the design of a transmission line where they are to be used. The power cables are not rigidly secured at each tower, as is approximately the condition with pin-type insulators, but they are supported at the lower ends of a number of chains which allow them to move horizontally for a certain distance in every direction. This movement not only increases the swinging of the cables when acted upon by wind at right angles to the line, making it necessary to allow greater

distances between phases, but the sags are seriously disturbed by the running of the slack in the cables from one span to another under certain conditions, which makes it very difficult to keep them from coming in contact with each other. Ice on the cables intensifies this difficulty, if they happen to be in nearly the same vertical plane, for the ice does not break away uniformly or simultaneously on all cables, but leaves some loaded, while others in the same span may be quite free. The resulting sags are very different in the two cases, and it can be imagined what a good opportunity for trouble exists.

With this type of insulator the upper part of the towers has to be greatly increased in size in order to obtain safe clearances between the tower members and the cables. Also it must not be overlooked that when the insulators are deflected to an angle of 50° to 55° from the vertical, the clearance between the cables and their respective cross-arms overhead is no longer equal to the length of the insulator, but is not much in excess of half this length. The obvious remedy is to either increase the length of the insulator or to droop the cross-arm.

As a further precaution it has become the practice to provide one or more ground cables above the power conductors to shield them from the effects of lightning. The results which have been obtained from their use have been quite satisfactory, but only very meager data are available quantitatively as to how much protection they actually afford. Whether more than one ground cable should be used is a point upon which opinion is divided, but the argument generally reduces itself to a question of cost, for it is agreed that if the transmission line were entirely enclosed in a metal cage, external lightning could have no effect upon it.

In closing this paper the writer wishes to add a few figures showing in a general way the costs per mile of transmission line construction suited to different voltages. These are based upon the use of copper cables of No. 000 B. & S. gauge (10.4 mm.) or their equivalent in aluminum. The market price of aluminum cables is generally lower than for copper cables of equal conductivity, but the advantage is offset by the necessity for using slightly higher towers with aluminum if the same clearance above ground at the middle of the spans is maintained, the need for

this being due to the latter metal's lower tensile strength and therefore the greater sags which must be allowed. These costs do not include a telephone line or right of way. It is assumed that the wooden poles are spaced 120 feet apart, and the steel towers 550 feet apart. In the total cost per mile 10 percent has been allowed for engineering and contingencies.

Description	Towers or Poles, Incl. Footings	Cables and Erection	Insulators	Total
12,000 volts.				
Pole Line—				
Double circuit.....	$1,400.00	$3,120.00	$ 130.00	$5,115.00
Single circuit.....	1,100.00	1,600.00	65.00	3,042.00
30,000 volts.				
Pole Line—				
Single circuit.....	1,400.00	1,650.00	200.00	3,575.00
60,000 volts.				
Steel Towers—			Pin Type	
Double circuit.....	1,800.00	3,300.00	220.00	5,852.00
Single circuit.....	1,630.00	1,700.00	110.00	3,784.00
110,000 volts.				
Steel Towers—			Suspension Type	
Double circuit.....	2,050.00	3,300.00	622.00	6,569.00
Single circuit.....	1,850.00	1,720.00	350.00	4,312.00

Based on copper, 18 cents per pound.

In the foregoing notes the writer has not touched upon the reliability of transmission lines in service, for the reason that with proper care in the design and selection of materials, especially insulators, coupled with the use of suitable protective apparatus, a modern line should give practically uninterrupted service. It must be borne in mind, however, that each particular case should be considered upon its own merits. For instance, an insulator may serve admirably on one line and fail utterly to give satisfaction on another of the same voltage. It must be added that this is most fortunate for some of us, for if it were not that each line built requires special consideration there would be but little need for the service of transmission engineers.

There is at the present time a matter of considerable interest in this connection, and that is the latest development in the gas power situation, namely, the use of Diesel engines operated by gas obtained from peat. It can easily be shown that the peat fields distributed over large areas of this country are far more

valuable to our power supply market than all our water powers, and, as water powers are frequently susceptible to severe interruptions, the utilization of peat as a fuel producer is worthy of consideration. It may even be that, in time to come, water power and peat power plants will be operated jointly, furnishing us with a permanent supply of energy, for, while water power plants may suffer during severe winter weather, the supply energy obtainable from peat is always available.

A paper presented in the Symposium on Power Problems in Electrochemistry, at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

SOME ECONOMIES IN THE USE OF ENERGY IN ELECTRIC FURNACES.

By F. A. J. FitzGerald.

The subject of economies in the use of energy, if thoroughly treated, would fill a long paper, giving many examples of electric furnace practice. The following remarks, however, will be merely an account of some general ideas on energy economy which have been evolved as a result of several years' experience with various commercial applications of the electric furnace.

The relatively high cost of the heat unit generated by means of electricity as compared with fuel has led all those interested in the development of electrothermics to give serious consideration to economies in electric furnace practice. While the end sought is most desirable, it is unfortunate that its pursuit has led to much misdirected effort, which, instead of realizing economies, has resulted in waste and consequent retardation of electric furnace development. This is not surprising, since the same thing is observed in the pursuit of many other desirable objects, such, for example, as conservation, efficiency, eugenics, etc. No one will deny that these things are important, and no intelligent observer can fail to see the vast amount of misdirected and even harmful activity generated in relation to them. Perhaps the most striking analogy to what I have in mind is found in certain activities for the relief of human ills. Recently there has been extraordinary agitation in favor of inducing the Government to take up the mining and manufacture of radium. Leaving out all such secondary motives as the creation of bureaucratic jobs, personal advertising, etc., it is found that many people, otherwise intelligent, believe, first, that cheap radium is one of the most important things for the welfare of the human race, and, second, that governmental meddling will result in the production of radium at a low cost. Now, as regards the first belief, we do not yet know the extent to which radium is applicable as a

curative agent, but, however important it may be, there is no doubt that its relative importance to human welfare in general is grossly exaggerated. As regards the second belief, even a superficial knowledge of the subject shows that, while governmental meddling may mean selling radium at a lower *price,* its production will be at a greatly increased *cost,* since in all lines of activity outside its proper functions there is no more inefficient and expensive machine than a government.

In electric furnace practice we have an analogous error which is made in the name of economy, first, in attaching an exaggerated importance to the saving of the heat units generated by the electric current, and, second, in the inefficient and expensive machinery used for the purpose, with the result that in slightly increasing the efficiency of the furnace there is a greatly increased loss of energy.

In attempting to realize energy economies in electric furnace practice the first consideration should be the conditions governing the cost of power, and this can be best illustrated by abstracting parts of a typical power contract:

1. The Power Company agrees to deliver so many horse-power 24 hours each day and every day in the year for a period of years.

2. In case the Purchaser's requirements are greater at times than the "firm" horse-power agreed to be taken and paid for, the Power Company agrees to supply such intermittent demands, but in that case the amount to be paid for is the average of the highest daily one-minute peaks occurring during the month for which the charge is made.

3. By "firm power" is meant the amount of power agreed to be taken and paid for by the Purchaser *whether or not he uses it.* By "intermittent demand" is meant the highest one-minute peak occurring during any one day.

4. The Purchaser must when possible take current equally from the three phases, but whenever it is impossible, and the difference between any two phases is greater than 10 percent of the lesser, he shall pay for power as though the current taken from each phase was equal to the greatest amount actually taken from any one phase.

5. The Purchaser must always maintain a power factor as near 100 percent as possible, but whenever this is less than 90 percent the average intermittent demand shall be considered as 90 percent of the maximum kilovolt-amperes taken for a period of one minute each day, except that the average intermittent demand shall never be considered less than the "firm" horse-power agreed to be taken and paid for.

The trouble with many—indeed, I may say, most—experimenters who are trying to start commercial plants, and even with some plants that are running commercially, is a failure to recognize the significance of the power contract. The important consideration in the plant, so far as energy economy is concerned, is that from the time the current is thrown on *100 percent of it must be used 24 hours each day and every day in the year.*

Instead of this consideration being the first one, it is continually neglected in the pursuit of some fad, such as increased efficiency in the use of heat units, or saving some waste gases, or working a complicated continuous instead of a simple discontinuous process. The result is that the exaggerated importance attached to these ends, desirable in themselves, leads to load factors far below 100 percent, or to peaks involving expensive intermittent charges, or to shutting down to repair or adjust complicated machinery built in the name of efficiency, while there is never any shutting down of the Power Company's bills.

A general review of electric furnace work during past years shows that a great waste has resulted from the efforts of inventors working on smelting problems, because they have attempted to develop elaborate schemes for preheating furnace charges, for utilizing CO gas to obtain preliminary reduction, etc., before they have thoroughly worked out the simple furnace problems free from efficiency devices.

The fundamental error of this work is the attempt to force too rapidly the natural evolution from the simple to the complex. Returning to our radium analogy, we have here another case of mistaken zeal in attaining an end desirable in itself, but relatively insignificant, so that much waste results from the use of cumbersome and inefficient machinery.

Another wasteful notion dear to the inventor is the continuous process furnace. In many cases continuous furnaces are apt to

mean complicated and expensive furnaces. One of these probably costs as much as several discontinuous furnaces. If an accident happens to one of the latter there is generally another ready to go on, but with the expensive continuous furnace there often is no spare one, or if there is it takes a long time to get it tuned up to normal working order, and meanwhile the power bill is eating up profits. The exaggerated importance attached to the continuous process has done harm in another way, for it has seriously retarded the development of processes for the utilization of off-peak power. This obviously requires discontinuous work, which has earned a bad name, thanks to the efficiency idealist.

Incidentally it may be mentioned that a preliminary study of the off-peak problem is distinctly encouraging; but I do not believe that it will ever be worked out until it is taken up seriously by those having power to sell, rather than by the customer.

After making sure that the consumption of power in a furnace plant will be continuous, the next step is to keep the power at 100 percent of that called for in the contract. In furnaces of which that used for making silicon carbide may be taken as the type there is, after starting, a rather gradual decrease in resistance, so in order to keep the power constant some means of regulating the voltage must be used. The cheapest way of doing this is to have a step-by-step method in connection with the transformers, but unless the steps are very close together it is not economical. A step-by-step device gives a load curve that looks like the teeth of a saw, and at the end of the year the energy wasted, represented by the spaces between the teeth, will pay for apparatus giving closer voltage regulation.

In arc furnaces we have extremely sudden changes of resistance, which should be taken care of by automatic regulators. These are very commonly looked on simply as labor-saving devices; but they are just as important as savers of energy. They avoid peaks—a fruitful source of expense—and keep the balance between the three phases. In a plant with which I am acquainted the installation of automatic regulation has increased the furnace yield somewhat over 10 percent.

As regards the question of power factor, this is not usually troublesome, except in the case of such an apparatus as the

induction furnace. In this case much may be done by the use of a suitable condenser. Thus very satisfactory results were obtained in the case of the American Electric Furnace Company's plant in Niagara Falls by the use of a synchronous motor with over-excited field coils. It was shown that in a plant of the kind running commercially the cost of the synchronous motor would be a good investment on account of the saving in the power bills.

As a final useful suggestion in relation to energy economies I may mention that in some cases it is possible to provide a furnace or furnaces to absorb any power which might otherwise be wasted for one cause or another.

I shall not take up any more of your time, though there are many other economies which might be considered. My main object has been to point out what I believe to be the general direction in which the quest for economy should go, and to give a word of warning about certain ideals which, however excellent in themselves, are apt to be exaggerated, with uneconomical results.

The FitzGerald Laboratories,
Niagara Falls, N. Y.

A paper presented in the Symposium on Power Problems in Electrochemistry, at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

POWER FOR ELECTRIC FURNACE WORK

By W. S. Horry.

The electrochemical industries are rapidly outgrowing the available supply of electricity generated by the natural water powers of this country, so that in the near future they must inevitably be carried on with power generated from coal by some kind of prime mover. It may be said that this condition of affairs is already confronting some of the electrochemists and must soon be met by many of the industries that have grown to large proportions in the last decade.

Most of these industries would never have been born but for the existence of abundant sources of electric energy made possible by the development of water power, and today there are many new processes invented, the practice of which is retarded until cheap electric power is more generally available. But now the abundant water power of a few years ago is already taken up, and the result must be that our electrochemical industries must extend elsewhere in other countries where natural water power is more obtainable, or else they must develop their electric power from coal.

This is now being done in England, at the home of the steam turbine, where large electrochemical works are being supplied with power from the mines, near which the turbine plant is built.

The extent to which the modern electric furnace requires energy is staggering. A single furnace some sixteen feet square will absorb 12,000 H. P. This amount of energy is sufficient for the light and power requirements of a city, so it will be realized that all the available water power, great as it is, will not suffice for the needs of the electrochemical industry much longer.

Our industries, too, are becoming more important. Many of them now feel able to develop the power they require, where, a few years ago, in consequence of the comparative novelty of their

business and the uncertainty and cost of so doing, the matter was not considered commercially feasible. Conditions are now ripe, therefore, for an enormous increase of power derived from coal for electrochemical uses, which bids fair to rank high among the other uses for which the electric current is generated.

It is fortunate for the continued development of our industries in this country that the production of electric power from coal has recently been so simplified and cheapened by our engineers. At the present time the cost of producing this power by steam is low enough to be considered as rivaling the cost where water power is employed under the conditions that generally rule in the practice of electrochemistry. This is another remarkable achievement of the otherwise remarkable age we live in.

The essentials for cheap power production from coal are close proximity to the coal mines, where plenty of water is available for condensing and where transportation facilities are adequate. The other requirements are met by the very nature of our processes. The load factor certainly will be 100 percent and the power factor, which also enters into the costs, can be kept round 93 percent at the switchboard even with the largest types of three-phase furnaces. Then, the first cost is kept down from the fact that it is not necessary to duplicate the generating machinery, modern boilers and turbines are quite reliable, and stoppages are remote and short and are such as not to constitute an objection for the purposes under review.

The actual prospective costs have been given by numerous contributors to fellow societies, such as Mr. H. M. Hobart, before the American Institute of Electrical Engineers. This author gives the investment cost as $35 per kilowatt for large powers generated at 60 cycles by steam turbine machinery and an operating cost of 0.25 cent per kilowatt hour as a minimum in cases where all conditions are favorable, and it is to be remarked that all conditions will at all times be favorable for such a plant in a properly chosen location, where electric furnaces constitute almost the entire load.

Mr. Hobart's paper is a recent one and must, therefore, supersede other estimates not so recent, because the operating economy of such plants is being improved year by year. So pronounced,

indeed, is this tendency at the present time that many large turbines only recently installed are now considered obsolete by their designers.

The paper alluded to has been criticised as giving the first cost too low, but in cases like these, where the whole design and even the location are secondary considerations to that of low first cost and low operating cost, this criticism will hardly apply, or, even if the figures should err a little on this side, they will correct themselves in a short time at the rate of monthly progress in such matters as is now the rule. If these costs are thought too low now, they may be thought too high very soon, because the last word in steam turbine and steam boiler design has not yet been said. We are not waiting for new inventions, but for the development of principles already understood, to secure progress in operating efficiency, and so, as higher pressure and higher superheating are used and more reheating practised, this progress is not a matter for speculation.

The 15 percent efficiency that Mr. Hobart assumes is daily being beaten and will most certainly be improved upon in the future. One criticism, that a 100 percent load factor may well be dismissed without discussion as a condition impossible of attainment, is, of course, wrong for a steam plant operating to supply electric furnaces. Then, the furnace itself has a power factor much higher than 95 percent and, when the conductors are designed to be as little inductive as possible, this can be realized in practice in a three-phase furnace of the capacity mentioned.

For electric furnace work the ordinary three-phase, twenty-five-cycle alternator meets all present requirements. Electrochemists have followed the lead of the electricians and have adapted their furnaces to the general scheme of power transmission. While single-phase transmission was the rule they conformed to that, though furnaces of large capacity were not possible with it. As the three-phase supply became more general, three-phase furnaces were constructed, and these mostly hold the field today for this work.

Although the twenty-five cycle system is adequate for the present requirements, the trend now seems to be to return to higher frequencies than twenty-five cycles for general distribu-

tion. Among the electricians the reasons are that the sixty-cycle converter has now been perfected, line inductance has been enormously reduced by the use of high transmission voltages and the transformers weigh less and are cheaper. But the fact remains that large three-phase furnaces are not possible with a sixty-cycle current, unless the electrochemist is prepared with new devices for keeping the induction down, since mere compactness of the circuit, so far relied on, is no longer adequate for this purpose. If it comes about that a sixty-cycle current is to be used for large smelting furnaces, the electrochemist must part company with the power electrician and develop a current of his own.

For the power of the three-phase, sixty-cycle furnace is limited. The cost of power is least when the power factor is unity. Therefore, good practice demands that this be kept high for the system as a whole and for the electric furnace in particular.

If we assume a power factor of 0.9, as measured on the high tension side of the transformers, and assume a delta voltage of 110, then the most power that a three-phase sixty-cycle furnace will take is about 2,750 kilowatt, though by special design this figure can be somewhat improved. This is quite low. The modern smelting furnace is of decidedly greater capacity, to facilitate the extraction of its products.

But, if this furnace be given six phases instead of three, it will take nearly double the power under the same conditions, while if twelve phases be chosen with twelve carbons in a ring at the furnace, then the power will be nearly four times that given, which would be sufficient for present requirements.

The six-phase secondary can be acquired by a mere change of the secondary connections from a three-phase transformer, and twelve phases can be similarly developed from two such transformers, one with its primaries connected delta and the other star fashion, the secondary voltages of the two being the same. Another function is then added to the transformers to increase the number of phases, as well as to lower the voltage, and, by this means, the even power produced from all dynamic machinery is reproduced within the furnace, although, for economical transmission, only three wires are employed in the line.

With these factors conceded, Mr. Hobart's figures look feasible to the writer. The cost of some 0.25 cent per kilowatt hour looks reasonably attainable in actual operation for a plant under the conditions existing in electrochemical processes. With these estimates before us, it looks as if the time was approaching when it will not pay to develop comparatively small water powers for this purpose, in an out-of-the-way district, away from markets, in a sparsely populated country and with high costs for transportation to and from the plant.

It must not, of course, be considered that the steam turbine is to have the entire field to itself in the electrochemical industry, even if it looks at present as if it was the only device commercially available for supplying 20,000 H. P. electric furnaces.

The gas engine has also been enormously improved in recent years and it cannot be safely predicted where these improvements will lead. The efficiency of these machines does not seem capable of improvement, taken alone, but means have been devised for utilizing the waste heat they eject to develop more power by steam. It is certainly the best prime mover in the steel trade, where blast furnace gas is available in great quantities.

Then the reciprocating steam engine has likewise advanced and holds the record today for coal economy in generating power. Combination plants have also appeared, in which each prime mover is allotted its most efficient stage of operation. Advance in such matters is so rapid that actual figures may not be given, but in general it may be said that the investment charges are higher than with the straight steam turbine plant, which stands quite alone in capacity and simplicity. In places where coal is expensive such refinements may be justified, but they are not justified in the electrochemical industry where the cost of electric power is of paramount importance and where everything else, even the location of the plant, is to be considered as secondary and subservient.

The actual cost of electric power derivable from a modern steam plant is not, however, the only point of view for the electrochemist. He requires coal for preparing the materials for the electric furnaces. In electrothermal work it pays to roast the ore to be smelted and it pays to dry and prepare the coal used

for reducing this ore. In other processes large amounts of coal are used to concentrate the solutions produced by electrolysis. Then it happens that a plant located where coal is cheap possesses advantages even if the cost of electric power from coal should be higher than that obtainable from a hydro-electric plant situated where coal is dear.

And, finally, there is always before the electrochemist the possibility of extracting the valuable constituents of the coal and of running the power plant with the residue. The by-product coke oven produces sulphate of ammonia, tar, coke and gas. The two latter are of use to him in his process, and, if the two former can be profitably sold, there would be a derived revenue that would operate to lower the cost of power. The scheme looks attractive for the reason that the by-products can be extracted only to the extent that this is profitable, while the raw coal can be served to the boilers if its treatment before use is undesirable.

A paper read at a meeting of the New York Section, January 9, 1914, in joint session with the Am. Inst. of Electrical Engineers and Am. Soc. of Mechanical Engineers, and called up for discussion in the Symposium on Power Problems in Electrochemistry at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

THE POWER PROBLEM IN THE ELECTROLYTIC DEPOSITION OF METALS.

By Lawrence Addicks.

Copper, lead, nickel, silver, gold, and some of the less common metals are now commercially refined by electrolysis. Lead, however, has such a large electrochemical equivalent that the power required is relatively small, and the tonnages of the precious metals refined are insufficient to demand special consideration. The electro-metallurgy of zinc is now being seriously studied, and the electrolytic refining of iron will follow upon any demand for pure iron as distinguished from the alloys commonly known as iron and steel. By far the larger proportion of the world's copper is electrolytically refined, and this work is almost exclusively an American industry, centered chiefly in large plants on New York Harbor. These plants are being steadily extended as the annual production of copper increases, and present a power problem well worthy of special attention.

A similar problem is beginning to arise in the leaching of ores followed by electrodeposition. Such work is now being inaugurated on a large scale in dealing with copper ores in Chile and around Butte, Montana. The energy used for deposition is much greater when insoluble anodes are used, as in the leaching propositions. With soluble anodes as used in copper refining, the voltage is almost entirely absorbed—to the extent of perhaps 95 percent—by the ohmic resistance in the circuit, and in general is about one-third of a volt per cell. With peroxidized lead or similar insoluble anodes working in sulphate solutions it requires about two volts per tank to maintain the same current density, owing to the chemical energy required to decompose copper sulphate at the cathode with no equivalent energy of formation developed at the anode. Where the anode reaction can be utilized, at least in part, as by the introduction of sulphurous acid which

is oxidized to sulphuric acid at the anode simultaneously with the deposition of copper at the cathode, an intermediate voltage will result. It is probable that large power installations for these leaching propositions will soon be required. The electrodeposition of zinc from liquors resulting from the wet treatment of complex ores is also receiving a great deal of attention, although the experiments have not yet reached as advanced a stage as in the case of copper.

Narrowing this whole question down to a copper refining plant as typical of this general class of electrolytic processes, we have the following power limitations imposed by present practice:

(*a*) Direct current.

(*b*) Say 8,000 to 15,000 amperes.

(*c*) Say 100 to 200 volts per circuit.

(*d*) Resulting in 800 to 3,000 kw. units—1,000 to 1,500 in present installations.

(*e*) Circuits electrically independent, to avoid cross leakage.

(*f*) Constant current; somewhat variable voltage—say ± 20 percent.

(*g*) Steady current load night and day.

(*h*) Steam needed for heating electrolyte.

(*i*) Plants of from 3,000 kw. to 9,000 kw. should be considered.

The reasons for these limitations are as follows:

(*a*) *Direct Current:* This is obviously required by the nature of the process.

(*b*) *Amperage:* This is fixed by the current density and the electrode surface per tank. (This paper considers only the so-called multiple system of refining, where the electrodes in a tank are in multiple and the tanks on a circuit in series.) The current density is fixed by a balance between the interest on copper tied up, the cost of power and the difficulties in practical handling of rough deposits.

Fig. 1 shows the approximate relation between cost of power and current density in American practice; the high densities, of course, call for cheap water power. Twenty amperes per square

foot of active cathode surface may be taken as representing practice in the vicinity of New York, with an ampere efficiency of 90 percent and an average consumption of about 1 kw. hour at the switchboard per 6 lb. (2.7 kg.) of copper.

Electrode surface per tank has been steadily increased until 30 pairs of electrodes, three feet (90 cm.) square, are used in one case. This calls for a current of 30 x 3 x 3 x 2 x 20 = 10,800 amperes. It is conceivable that higher densities and longer tanks may come into use, so that I have placed the practical limit at 15,000 amperes, but 10,000 amperes should be taken for a definite discussion.

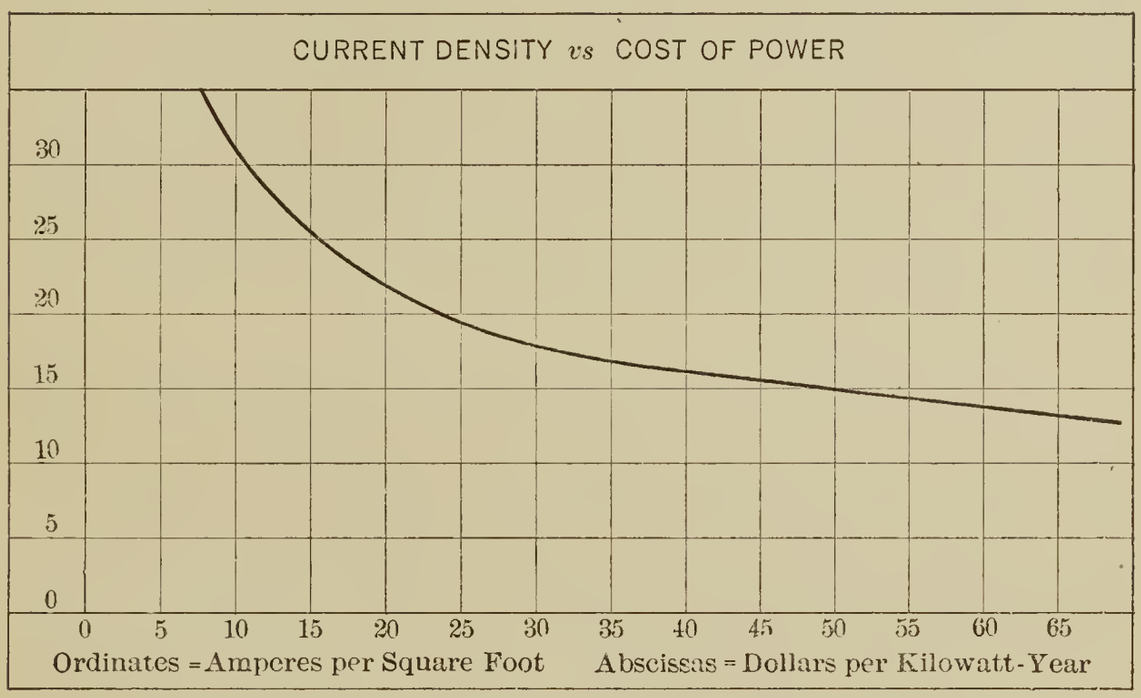


FIG. 1.

(*c*) *Voltage:* As we have to deal with a highly conducting electrolyte, containing 10 to 13 percent of free sulphuric acid, which must be continually circulated to avoid stratification in the tanks, carefully studied construction is necessary to avoid serious trouble from leakage currents. These not only represent wasted energy, as shown by the so-called current efficiency, but wherever current jumps from the electrolyte to a lead pipe or other metallic conductor, a rigidly equivalent quantity of copper is deposited thereon and when traversing acid-soaked wood of relatively high resistance, a quantity of heat sufficient to cause a fire risk may be generated. It must be remembered that nearly the entire electrical

energy produced at the generators appears as heat in the tanks. It can be readily appreciated that high voltages greatly aggravate these difficulties. While I have suggested 100 to 200 volts as the range per circuit, I favor the lower limit and do not believe voltages higher than 150 to be good practice.

(*d*) *Kilowatts:* 10,000 x 150/1,000 = 1,500 kw. for our typical case. This is a little larger than most of the units at present installed, but represents the probable size for a new installation.

(*e*) *Circuits:* The statements already made regarding current leakage indicate the undesirability of any electrical connection between generators, and I believe it would be necessary to use motor generators instead of rotary converters in any A.C.—D.C. scheme distributing power from a large unit over several circuits.

(*f*) *Uniformity:* The first principle to be observed in the operation of an electrolytic refinery is uniformity of conditions. The process is very delicate and, while simple in theory, economy depends upon the successful balancing of many conditions to obtain the best results.[1]

In consequence, the current should be held at a fixed value, following variation in the resistance of a circuit with the voltage. Hand control of the field of shunt wound generators is adequate, as the changes in resistance are very gradual. An exception to this statement is the case of cutting out sections of tanks for several hours when drawing copper. It is also necessary to carry up to 2 percent insoluble-anode tanks, to correct the gradual accumulation of copper in the electrolyte, and as these require about six times the normal voltage for operation, they cause an appreciable variation in the total resistance of the tank house when they are added or withdrawn. To cover this range a field control of our typical generator from 120 to 180 volts at 10,000 amperes will be required. Of course there will be times when partial or excessive loads will be carried to meet slack or congested supplies of copper, but these conditions are not normal and need not be met with economy.

(*g*) *Load factor:* The operating conditions as described amount to practically 100 percent load factor for both momentary and 24-hour loads.

[1] Transactions American Electrochemical Society, **5**, 119 (1904).

(*h*) *Warming electrolyte:* Electrolytes have a high positive temperature coefficient of conductivity. As this amounts to about 0.5 percent per degree F. (0.9 percent per 1° C.) and as the electrolyte represents about half the ohmic resistance of the circuit, it is evident that its temperature must be considered. In general, the electric energy dissipated in the tanks will maintain a temperature of 90 to 100° F. (32°–38° C.) and it has been found economical to add sufficient steam in closed coil heating tanks to keep the circulating electrolyte at an average temperature of about 130° F. (54° C.). Exhaust steam can be used, and roughly an amount equivalent to one-fourth of the steam supplied to the engines is required. Additional steam is required for light and power, compressed air, pumping and the manifold requirements of a refining process of which electrolysis is but one step, so that figuring for the moment on the use of live steam for heating the electrolyte, only about one-half the total boiler capacity is used for electrolytic power generation. On the other hand, waste heat boilers attached to the reverberatory furnaces which form a necessary part of every refinery will generate more than enough steam for heating the electrolyte and any other uses where steam, as such, is essential.

(*i*) *Size of plants:* American copper refineries vary from 4,000,000 lb. to 35,000,000 lb. (1,800 to 16,000 metric tons) monthly capacity. At 6 lb. (2.7 kg.) per kw. hour our 1,500 kw. generator would take care of 6,500,000 lb. (3,000 metric tons) per month. Eliminating the smaller plants and allowing for some future extension of the larger ones, we would consider from 2 to 6 circuits of 1,500 kw. each, or 3,000 kw. to 9,000 kw. equivalent to from 13,000,000 to 39,000,000 lb. (6,000 to 17,500 metric tons) copper per month.

Turning now to present practice in the vicinity of New York, we find a very cheap source of fuel in No. 3 anthracite "buckwheat" at $1.75 per long ton ($1.715 per metric ton) delivered. Using this fuel, steam can be produced for about 15 cents per 1,000 lb. (33 cents per metric ton), including all operating expenses, but excluding administration, taxes, depreciation and interest charges. With this base price for steam, a kilowatt hour can be safely figured at 0.4 cent on a similar basis, allowing for

auxiliaries and a reasonable departure from ideal conditions in everyday operating. In fact 0.3 cent can be approached with first-class conditions.

Present practice is to use moderate superheating and vacuum, with the highest grade reciprocating engines. At the Raritan Copper Works four cylinder Nordberg triple expansion engines have recently been installed, while at the Chrome plant of the U. S. Metals Refining Company a triple expansion unit using a compound Hamilton-Corliss engine with a Rateau turbine for the third expansion is being tried out. Previous installations have

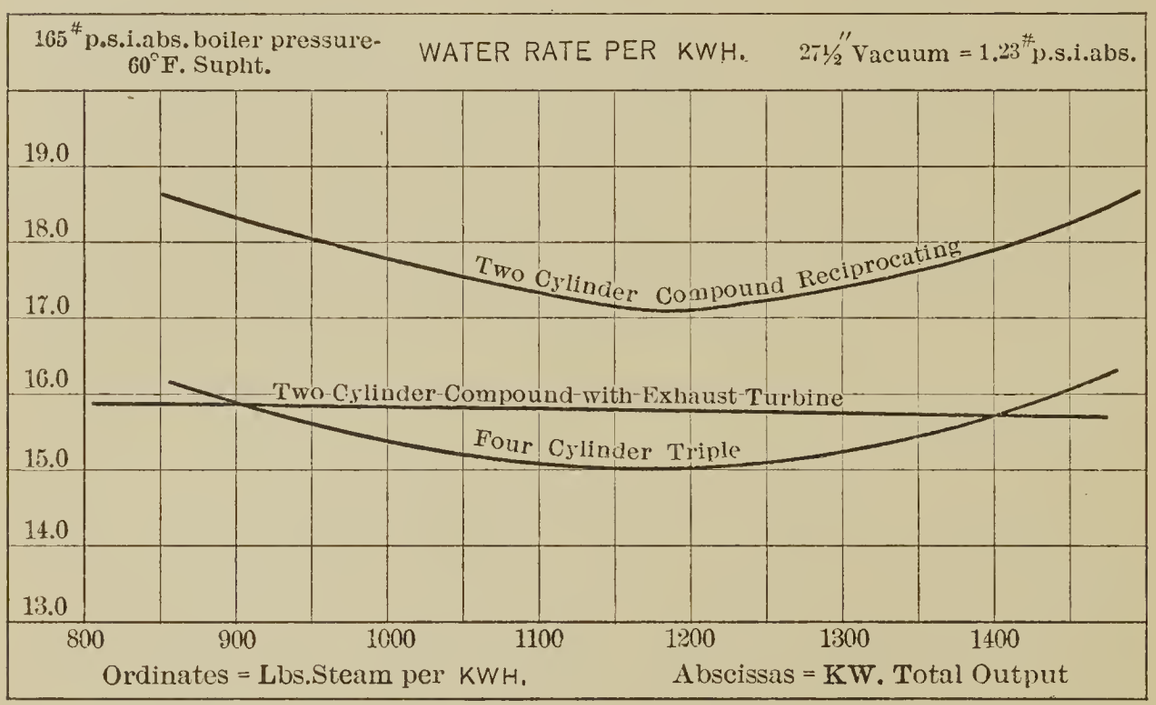


FIG. 2.

been chiefly confined to compound condensing units. Final figures for these recent installations are not yet available but Fig. 2 shows about what can be expected from a 1,200 kw. unit of each type, excluding steam for operating condenser.

The Chrome installation is of particular interest on account of the successful commutation of 6,000 amperes (the engine generator and turbo-generator running in parallel) at 1,500 revolutions per minute by a Rateau-Smoot generator.

The installation cost of such power plants may be roughly taken at $100 a kilowatt, including the disproportionate boiler equipment and auxiliaries.

The plant of the future may consist of gas-driven units, of large capacity A.C. turbo-generators driving motor generators of smaller size, of compound reciprocating engines exhausting into a trunk main from which exhaust steam turbines are fed, of multiple expansion reciprocating engines, of turbine driven unipolar generators, or of some combination of these. Spare units must be provided in sufficient proportion to give absolute reliability of service.

A paper read at a meeting of the New York Section, January 9, 1914, in joint session with the Am. Inst. of Electrical Engineers and Am. Soc. of Mechanical Engineers, and called up for discussion in the Symposium on Power Problems in Electrochemistry at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

THE POWER PROBLEM IN THE ELECTROLYTIC DEPOSITION OF METALS.

By H. E. Longwell.

You will pardon me if I confine myself to a general comprehensive survey of this problem from the hill top of common sense, instead of approaching it by numerous narrow paths, more or less disconnected, which lead up only to individual details. It is not enough that details are excellent in themselves; we must consider their fitness for co-operating with each other in such a way as to form a well-balanced and efficient unit. Furthermore, we must not let our enthusiasm for excellence in one detail tempt us to ignore the question as to whether the degree of excellence we are striving for justifies its cost, or whether or not it is worth while at all.

If we are planning civic improvements, we should not carry the gratification of our artistic sense to the point where we must sacrifice sanitation and education. If one is designing a speedy steamship, he must be careful to stop short of that degree of speed that demands a sacrifice of reasonable safety and staunchness in the construction of the hull.

Or to come to a more pertinent illustration, if one is designing a power plant, he must not become so obsessed with the question of mere steam economy that he will spend a dollar to save ten cents' worth of steam, or that he will spend ten cents to save some steam that costs him nothing at all.

It is not such an unusual experience, as one might think, to find people, intelligent people at that, who see the power problem with such a distorted perspective that the single item of the steam consumption of the prime-mover hides everything else in the field of vision. I recall two cases that were especially typical: one a wagon works in the West, and the other a textile mill in

New England. Both were using single-valve high-speed steam engines of a type that I have every reason for regarding with respect and affection, but which has been frequently and slanderously characterized as a "steam eater." The manager of the wagon works admitted that he was getting reliable operation from his engine with a minimum expense for upkeep. However, some one in whom he had implicit confidence told him that a Corliss engine would do the work with 25 per cent. less steam, and he was appalled by the apparent ruinous waste. Now this works includes some acres of dry kilns which required much more steam than the total exhaust of the engine. In fact, it was practically impossible to detect any measurable difference between the fuel consumption on Sunday, when the engine was not running, and the consumption for any regular working day. The fuel was all refuse from the wood-working machines and there was always a surplus which had to be burned in a destructor. By patiently reasoning with the manager for a little while, he was able to see that if saving all of the steam used by the engine did not effect any noticeable reduction in the total fuel consumption, it would be hopeless to expect to detect the economic benefits accruing from a saving of 25 percent of it. And finally it dawned upon him that even if he could save a measureable quantity of fuel by installing another engine, his only return for the increased investment would be the joy of burning up his savings in the refuse destructor.

The textile mill mentioned engaged a new superintendent, and he could see nothing ahead but bankruptcy unless the wasteful high speed engines were replaced by a compound condensing engine. In this mill sundry washing and dyeing operations used up all the exhaust of the engines, and some live steam besides. I am happy to say that before committing any blunder the new superintendent was gently and skillfully assisted to an understanding of one fundamental principle of power plant economics; to wit, if all the exhaust steam from an engine is required for some useful purpose, that engine is furnishing power with an efficiency of 100 percent, and any expenditure with the object of bettering that efficiency is not likely to be a temptingly profitable investment.

The two instances I have mentioned date back so many years

that I can relate them now without running much risk of hurting the feelings of any one.

If it were not in bad taste to do so, I might cite several modern instances that are equally comical—or perhaps *sad* would be the better adjective to use.

I have the honor of being acquainted with an efficiency engineer—a *real* one, who was gracious enough to answer my somewhat impertinent question as to how one man could be a reasonably efficient advisor to all men in all lines of work. He said that the thing was possible because scarcely any of the problems submitted to him involved special technical knowledge, but that practically all of them could be solved readily by the exercise of plain common sense.

In dealing with any technical problem, common sense is most useful, and common sense combined with special technical knowledge is doubtless better; but technical knowledge without common sense is disastrous.

I have laid some emphasis on the fallacy of attaching too much importance to the question of mere fuel economy in a power plant, because I think I detect just a little tendency in this direction in the very lucid and able presentation of the problem that has been submitted as a foundation for this discussion. Sundry estimates are submitted as representing the probable cost of steam and electrical energy, *exclusive of administration, taxes, depreciation and interest charges.*

The items of interest, taxes, insurance and depreciation—or to speak more exactly, amortization—are too important to be ignored. These so called fixed charges, or investment costs, are in general greater in amount than the total cost of labor, operating supplies and maintenance. They are especially significant in that they measure the cost of fuel economy.

To illustrate, let us consider the probable comparative performances of a high-grade steam-turbine plant, and a gas-engine and producer plant, consisting of several 1,500 kw. generating units. The electrolytic refining industry offers any investment in the interest of economy an unusually favorable opportunity to "make good," because the investment is permitted to work at its utmost intensity 8,760 hours per annum, and once every four years it is allowed to put in 24 hours overtime.

Assuming the fuel to be the highest grade of bituminous or semi-bituminous coal, having a calorific value of 14,500 B. T. U. per pound (8,055 calories) the gas engine and producer plant would, under test conditions, effect a saving of one-half pound (0.23 kg.) of coal per kw. hour over the turbine plant, or say two tons per annum. If the coal cost as much as $3.00 per ton this would mean a saving of $6.00 per kw. year.

The gas-engine and producer plant will cost about $50 per kw. more than the steam-turbine plant, and the question arises as to whether it is worth while to invest $50 in plant to save $6.00 a year.

Naturally there will be differences of opinion as to what would constitute an attractive return on this extra investment. For my own part, I should want six percent for interest, one percent for taxes, one percent for insurance, and two percent for maintenance. Having due regard to the appalling speed with which new things in engineering become old, I shouldn't feel comfortable unless I had a sinking fund of eight percent to provide for the safe return of my capital. The sum of these items amounts to eighteen percent. Even with the gross return assured, I think I should be inclined to regard a six percent farm mortgage as a more attractive investment. In my own opinion—from which you have every liberty to differ—the gross return should be not less than twenty percent per annum, so that this saving of $6.00 per kw. year would be too expensive if it required an extra investment of more than $30 per kw. in plant equipment.

In thus calling attention to the importance of investment or fixed charges as a factor in the cost of power, I am only touching in a very superficial manner on the doctrine that has been ably and vigorously preached and assiduously practiced by Mr. Henry G. Stott, who as you know is most prominently identified with at least two of the societies participating in this joint meeting.

The determination of the cost of electrical energy is a large subject, and those who are interested in it will profit by reading a paper entitled "Standardization of Method for Determining and Comparing Power Costs in Steam Plants" which was presented jointly by Mr. Stott and Mr. W. F. Gorsuch, at the June, 1913, meeting of the American Institute of Electrical Engineers, and

which is published in the May, 1913, issue of the proceedings of that society. This paper is particularly happy in its treatment of investment costs.

With respect to the type of power-plant best suited for the electrolytic refining of copper, I think we may safely eliminate the gas-engine equipment from serious consideration.

The plant will naturally be located in a place where there is an abundant water supply available for condensing purposes, and where the cost of fuel is reasonable. In other words, we may choose a location where the conditions are such as to enable a steam plant to display its best economy. Under these conditions, as I have pointed out before, the gas-engine plant would be a doubtful investment, even were there no especial reason why it is not desirable for this particular class of work.

There appears to be one reason why the proposition is peculiarly one for a steam plant, and in dealing with this point it is to be understood that I must base my discussion on premises supplied by those actively engaged in electrolytic copper refining, and which are matters that could not come within my own personal experience.

According to Mr. Addicks' statement of the problem, if live steam were used for heating the electrolyte, the total steam from the boilers would be used as follows:—One-half for electric power generator, one-quarter for steam-driven auxiliaries, and one-quarter for heating the electrolyte. Steam-driven auxiliaries are not as a rule so efficient that they abstract any serious amount of heat from the steam passing through them, so that for the purpose of heating the electrolyte the exhaust from these auxiliaries would be practically as effective as an equal quantity of boiler steam. Therefore the boiler steam required for auxiliaries and for heating the electrolyte would be approximately fifty percent of the amount required for generating the electric current.

I am informed by the general manager of one of the largest refineries in this country, that in a plant having an output of 500 tons of refined copper per day, the waste-heat boilers connected to the reverberatory furnaces, forming a part of such a plant, should be capable of supplying 50,000 pounds of steam per hour. This is somewhat over 40 percent of the steam re-

quired by the main generating units, or practically enough to operate all of the auxiliaries that would usually be run by independent steam motors in a steam-driven plant, and the exhaust from these auxiliaries would take care of the heating of the electrolyte.

This quantity of steam is too important to ignore, and even though gas-engine-driven main generating units were installed, it would be necessary to make use of this steam from the waste heat boilers.

The practical difficulty arises, as I understand it, from the fact that while the tanks are operated continuously, it is not usual to run the furnaces on Sunday. Consequently it would be necessary to have a considerable boiler plant in reserve to be operated only one day in each week for the purpose of tiding the plant over Sunday. And so even if there were no question as to the commercial economy of a gas-engine and producer plant as a general proposition, this one practical operating condition would be sufficient to rob it of all its theoretical advantages.

In a steam plant the regular boiler equipment is so flexible that it will readily take care of the fluctuations in the output of the waste heat boilers. Since with modern mechanical stokers it is not unusual to force boilers to 200 and 300 percent of their normal rating, it is evident that no decidedly disproportionate boiler capacity would be required to carry the plant over the weekly interval in which the waste heat boilers are out of commission.

The combination of a compound reciprocating engine exhausting into low pressure condensing turbine looks on first consideration to be inviting, since it is generally admitted that between the limits of the usual boiler pressure, and atmospheric exhaust pressure, a reciprocating engine is usually more efficient than it is customary to make the portion of a complete expansion turbine that takes care of this part of the pressure range. While the superior fuel economy of this combination seems very apparent from purely theoretical considerations, there is comparatively little available information regarding its amount in actual figures.

It is not denied that this combination has its legitimate uses, but it is most certain that mature judgment is required for determining the conditions under which it may be recommended and

it is equally certain that the combination has been installed in a number of instances in which its use was decidedly ill-advised.

Admitting the hypothetical economy of the combination, let us consider the features that tend to offset this advantage.

We have firstly increased initial cost. A low pressure turbine will in many instances cost 75 to 80 percent more per kw. than a complete expansion turbine. That this is reasonable may be readily seen by an inspection of Fig. 1, which is a sectional view through a typical expansion steam-turbine of the Parsons type. Let us assume that the capacity of this machine is 3,000 kw. What must we do to convert this 3,000 kw. turbine into a low pressure turbine of half this capacity. We simply cut out that portion included between the two vertical lines A B and

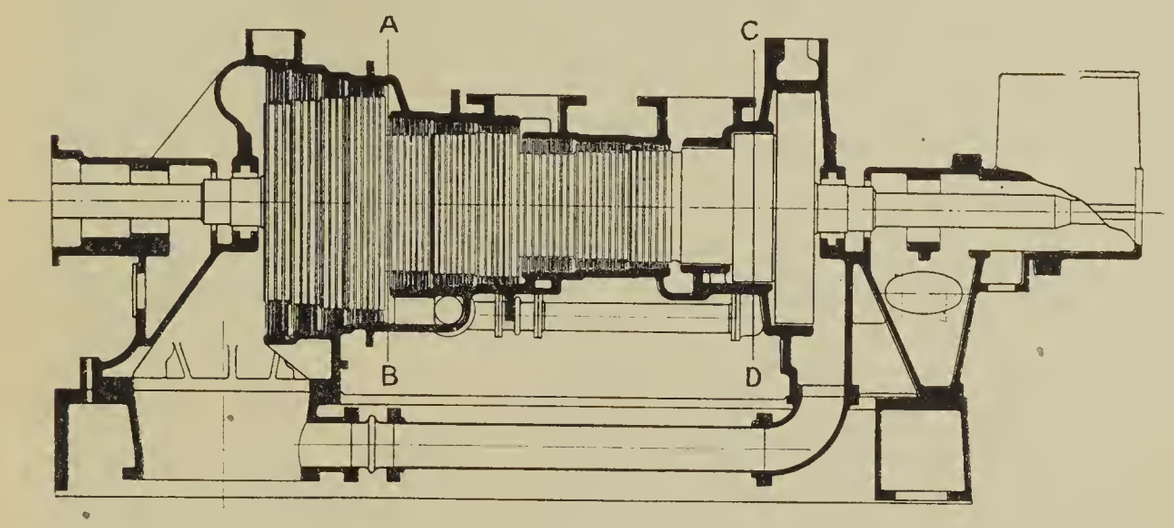


FIG. 1.

C D, and increase the inlet opening some six or eight times. Now it does not require any unusual qualifications to enable one to see that the part eliminated does not by any means represent one-half of the cost of the 3,000 kw. machine. Neither would any one of reasonable intelligence expect to purchase 1,500 kw. capacity in a reciprocating engine for any sum remotely approaching the cost of the section that has been eliminated from the complete expansion turbine. Again, no one would seriously claim that the expense of installing the combination unit would be less than twice that of installing the single complete expansion unit, and no one would be hardy enough to suggest that the charges for attendance, maintenance and operating supplies would be approximately equal for the two units.

There are, doubtless, cases in which the possibility of conserving reciprocating engines already in use would justify this combination type of unit, but in a plant that is new throughout its desirability is, to say the least, highly problematical.

As far as actual authoritative figures giving the comparative power costs for the two types of unit are concerned, I am sure that Mr. Stott could give us these if he would. The most important installation of combination units in the world was carried out under his direction. He had the justification of conserving valuable reciprocating engine equipment which was in excellent physical condition, and there can be no question that the best possible engineering judgment was exercised in designing and executing the project. I am confident that Mr. Stott has accurate and comprehensive costs of electrical energy as generated by this plant, and that these costs represent the utmost possibilities of this type of unit. If Mr. Stott would be willing to say whether or not in an absolutely new plant he would seriously contemplate the installation of combination reciprocating engine and low-pressure turbine units, such a pronouncement would be more convincing than volumes of argument based purely on theoretical grounds.

As regards the comparative merits of compound and triple expansion reciprocating engines and turbines as prime movers the trend of general practice in power plant design shows pretty conclusively that the turbine has the advantage. It has economic possibilities at least equal to those of the reciprocating engine, and markedly better when working with the high vacuums obtainable with the newer types of condensing apparatus and the copious supply of cooling water that is invariably found in places that would be regarded as favorable locations for electrolytic copper refining plants.

I speak of the economic *possibilities* of a certain type of prime mover rather than of its inherent economy, because the latter is not inseparably associated with the type. A prime mover is not economical simply because it is a compound engine, a triple expansion engine or a turbine, but because it is economical by design. There are hundreds of triple expansion engines that are less economical than some compound engines. In fact I am not sure that there are authentic records of triple expansion

engines which show sufficient improvement over the economic results of the best examples of two cylinder compound engines to justify the added complication and expense of the third cylinder and its connections.

It is possible to design a turbine that will be less economical than a very ordinary multiple expansion reciprocating engine. On the other hand turbines are built that under suitable operating conditions give economic results that cannot be equalled by reciprocating engines of any type, however skillfully designed, if operated under the same conditions.

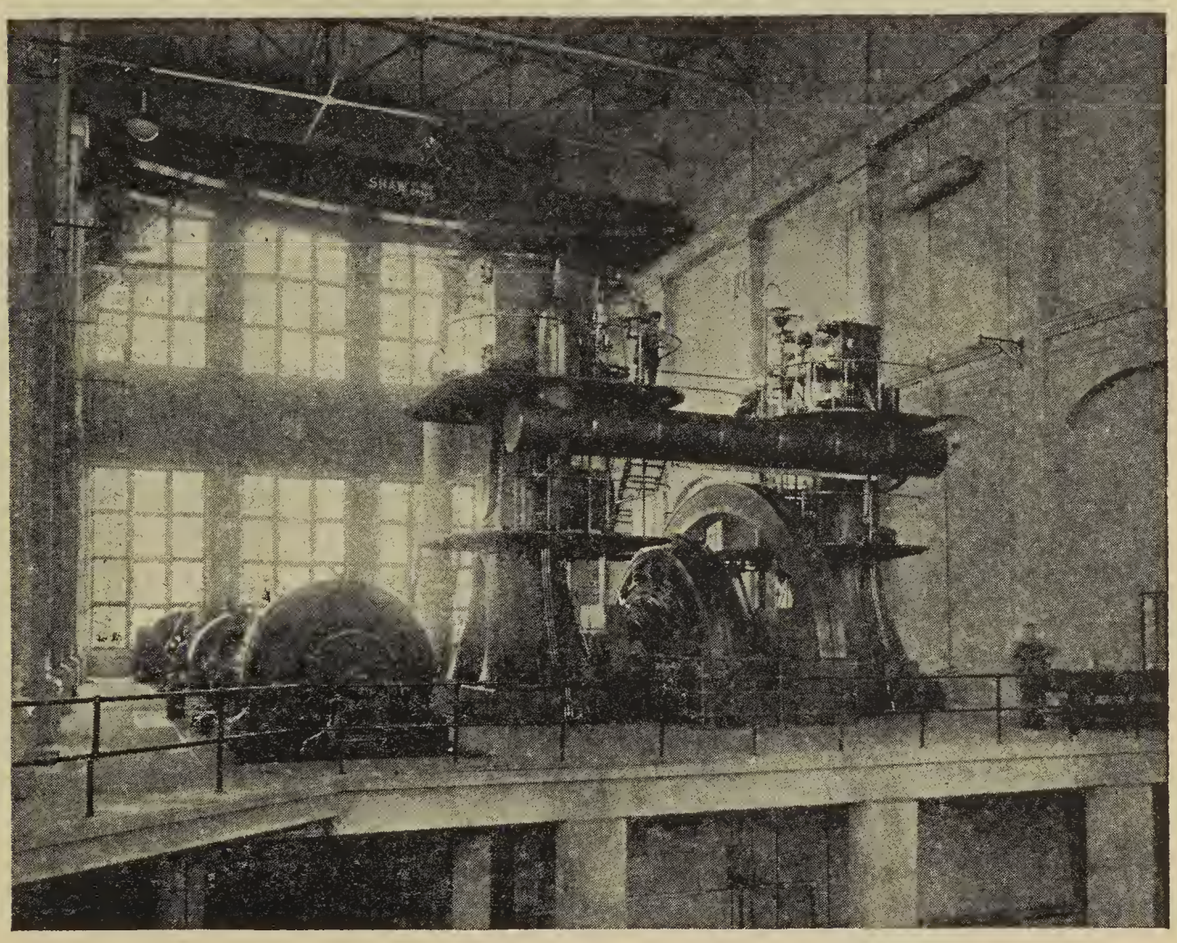


FIG. 2.

The advocates of the turbine can afford to be unnecessarily modest, and claim no more than equality with other types of prime mover as regards steam economy, for there remain still the unquestioned advantages of lesser cost, and smaller installation expenses.

For some years the turbine was at a disadvantage in plants in which it was desirable to generate direct current, for the

reason that the rotative speed of an efficient steam turbine, and the rotative speed of a reliable, efficient, direct-current generator are not compatible. This disability has happily been removed by the development of a reliable transmission gear, which allows any reasonable speed ratio between the turbine and the generator.

This gearing has an efficiency of over 98 percent, and has been in public use long enough to demonstrate that in point of reliability and durability it is at least on a par with any other kind of apparatus forming a part of an electric power plant.

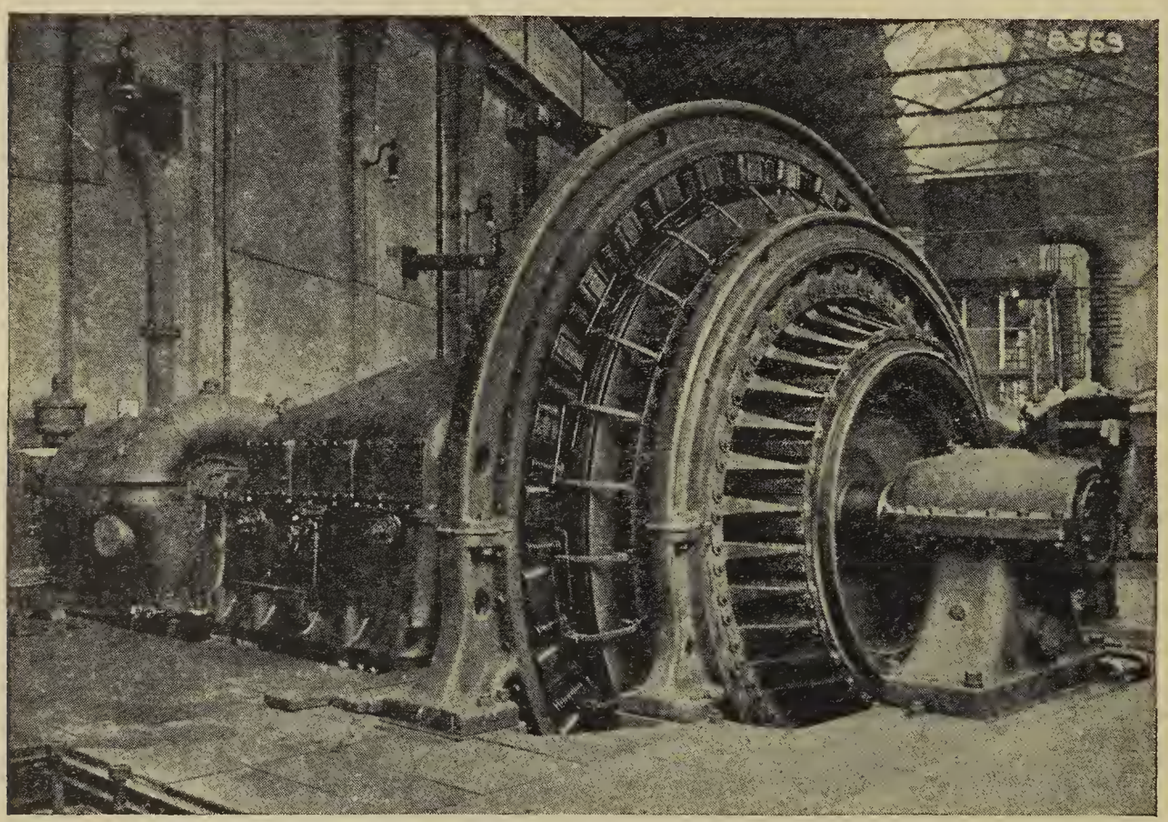


FIG. 3.

Figure 2 is a view of one of two 1,500 kw. geared sets installed at San Diego, Cal. The illustration gives a good idea of the size of this unit as compared with an engine-driven set of approximately the same nominal capacity. One of these sets was in regular service two years on the third day of last September, and the second will have been in service two years on the fifteenth day of next month.

Figure 3 shows one of two 3,000 kw. geared D. C. turbo-generator sets installed for the Cleveland Electric Illuminating Company. One of these sets was put in service a year ago on

the 6th of December, and the other a year ago on the 20th of the present month. It is fair to say that in this case the exhaust of the turbines is used for district heating, and the units operate only during the heating season.

Figure 4 shows a smaller set, 750 kw., owned by the Louisville & Nashville R. R. Company, which has been in service just about one year.

In addition to the sets illustrated, I might mention six others of 750 and 1,500 kw. capacity, all of which have been in regular service for more than two years, and the oldest of which will have been in service three years on the fourth of April next.

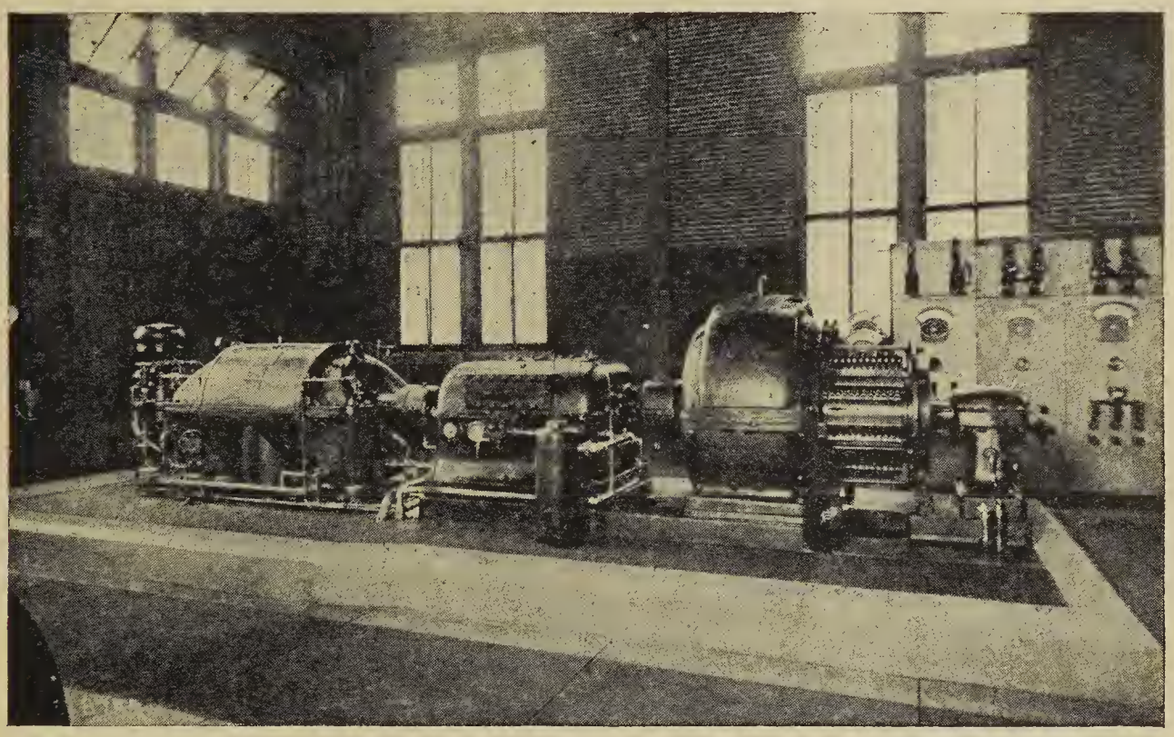


FIG. 4.

While the geared D. C. unit costs more than an A. C. turbo-generator unit of the same capacity, it is cheaper and somewhat more efficient than the combination of an A. C. unit and rotary converter.

I am not in possession of reliable costs for compound reciprocating engine-driven units, but commercial experience indicates that the geared turbine-driven unit has an advantage as regards price f. o. b. at the factory. With freight and installation costs added, the advantage is obviously more marked.

Figures purporting to give probable plant and unit power costs

are as a rule unsatisfactory because they are affected by too many variable factors. As regards plant cost, it might be said that depending on the expensiveness or simplicity of one's architectural tastes, his luck in selecting a contractor, his resourcefulness as a designer, his *finesse* as a buyer, the accessibility of the site selected, the state of the weather, and a lot of other things, he ought to be able to build a really good turbine-driven plant of from 6,000 to 9,000 kw. capacity, for $75 per kw.—more or less.

As regards the cost of power: if one is satisfied with investment charges of 10½ percent per annum, if he can buy really good coal at not over $3.00 per ton, if he is a capable manager and a careful operator, and reasonably economical, he ought, with a plant of this size, to be able to produce a kw. hour at the switchboard, with substantially 100 percent load factor, for four and three-tenth mills ($0.0043)—also subject to the qualification "more or less."

A paper read at a meeting of the New York Section, January 9, 1914, in joint session with the Am. Inst. of Electrical Engineers and Am. Soc. of Mechanical Engineers, and called up for discussion in the Symposium on Power Problems in Electrochemistry at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

SOURCES OF DIRECT CURRENT FOR ELECTROCHEMICAL PROCESSES.

By F. D. Newbury.

The electrical power problem involved in all commercially important electrochemical processes is the production of very large amounts of direct current energy at comparatively low voltages. Single circuits often require as much as 10,000 amperes, and in electrolytic processes the voltage is rarely more than 250 volts. The present paper will briefly outline the problem, list the various methods of obtaining the required electrical energy and compare these methods from the standpoints of efficiency, first cost and reliability in operation.

The electrical problem is intimately connected with the available prime movers and their advantageous operating speeds. In modern installations, steam turbines and water wheels with their relatively high speeds are of major importance. Reciprocating steam engines are of importance mainly in combination with low pressure turbines. Up to the present time, gas and oil engines have had little or no application in modern electrochemical plants, but the present rapid development of the Diesel engine abroad may make its influence felt in the near future.

The design of direct current machinery, either generators or rotary converters, of sufficient current capacity for electrochemical work is a problem of considerable inherent difficulty because of the large currents involved, the high speeds of the preferred prime movers, and the continuous full load service required. In some cases, as in A. C. turbo-generators, the low voltage involved may become a serious limitation in design aside from its association with the large amperage.

The large currents and high speeds are closely associated, and may be discussed together as the *commutation problem.*

The Commutation Problem.—In direct current generators and rotary converters the *speed* and the permissible *number of poles* bear a certain relationship; the product, in terms of revolutions per second and pairs of poles, is the *frequency*. In rotary converters this is, of course, a rigid relationship due to their synchronous operation. In direct current generators, the frequency is commonly lost sight of, but at the higher outputs and higher speeds under consideration it is practically as important a limitation as in rotary converters. The *current output* in commutating machines is proportional to the number of parallel circuits in the armature, which in turn is equal to the number of poles. The tendency, therefore, is to increase the number of poles indefinitely as the required current output is increased. But this indefinite increase is limited, to mention only the most important factors, by the number of current collecting brush arms that can be placed around the commutator and the number of commutator bars that can be placed between brushes without exceeding safe commutator peripheral speeds. If conservative design limits are not to be exceeded, it is necessary to keep the frequency within 60 cycles and desirable to keep it within 50 cycles.

With the maximum number of parallel circuits and poles that can be used, the total current output is then limited by the permissible length of commutator. At the higher commutator peripheral speeds required by the frequencies usual with the D. C. generators under consideration, 800 amperes per brush arm is as high as should be considered under the continuous service required by electrochemical processes. Lower values are commonly used in 60 cycle rotary converters and higher values are permissible in 25 cycle converters, the peripheral speeds being respectively higher and lower. Uniformly higher values can be safely used for the intermittent service commonly experienced in industrial plants and central stations. Higher values can also be used in very low voltage machines using metal instead of carbon brushes.

With these none-too-conservative limits of 50 cycles and 800 amperes per brush arm, the following maximum current outputs are obtained for 250 volt direct current generators for the range of speeds commonly used:

Prime Mover and Generator Speed	Poles	Frequency	Amperes	K. W. at 250 Volts
1,800-1,500	4	60-50	1,600	400
500	12	50	4,800	1,200
400	16	53	6,400	1,600
300	20	50	8,000	2,000
250	24	50	9,600	2,400
200	30	50	12,000	3,000
175	34	49.5	13,600	3,400
150	40	50	16,000	4,000

Larger outputs than those listed have in some instances been obtained at certain speeds, but only at the expense of reliability in operation. This is particularly true of direct-connected direct-current turbo-generators.

Double commutator generators, if used, would double the above ampere and kw. limits, but difficulties inherent in parallel operation of the circuits from two commutators connected to the same winding have, after several unfortunate attempts, caused this construction to be abandoned for large machines where conservative practice has been followed.

It is evident from the above discussion that the major difficulties in building generators and rotary converters for large currents center in the mechanical design of the commutator. The peripheral speed is pushed to the highest limit to obtain room for as many poles as possible; the length of commutator face is made as long as possible to increase the permissible current per circuit to the limit.

Three constructions have been developed and are in more or less general use to meet these severe conditions.

(*a*) A modification of the ordinary V-ring construction involving an additional auxiliary V-ring at the outer end of the commutator.

(*b*) A modification of the ordinary V-ring construction involving a shrink-ring midway between the two ends of the commutator bars.

(*c*) A simple shrink-ring construction involving two or more shrink-rings, depending on the length of the commutator.

The so-called three-V-ring type retains all the advantages, from the repair standpoint, of the simpler two-V-ring type. The combined V-ring shrink-ring type has the disadvantages from a repair standpoint inherent in the simple shrink-type. These two

types are comparable in their range of application. Such commutators have been built 20 in. to 25 in. (50 to 63 cm.) face and 5,500 feet (1,680 m.) per minute peripheral speed. The simple shrink-ring type obviously does not permit of easy repair and is limited to comparatively small commutator diameters. It is, however, the strongest construction available for smaller diameter commutators and is necessarily used for direct-connected turbo-units.

Improvements in commutator design and construction during the past four or five years have been largely instrumental in improving the operation and extending the permissible output of the generators and rotary converters under consideration.

A word in regard to the operation of machines having long high-speed commutators is not out of place. Such commutators are built up, in part, of more or less compressible insulating material, and require a period of "seasoning" and adjustment before they will operate without further change in shape. A certain amount of such seasoning occurs during the manufacture and test (where testing is possible) of the machine, but it is very seldom that additional grinding and tightening is not ncessary after installation.

The Distribution Problem.—Energy in the form of heavy currents at comparatively low voltages, as used in electrochemical work, is not efficiently transmissible; it must be used substantially where it is generated. Very heavy bus-bar structures, expensive both in first cost and in energy loss, are necessary to carry the large current from the generator to the point at which it is used, and for distances more than a few hundred feet the cost becomes prohibitive. For transmission distances of 1,000 ft. (300 m.) or more, it is usually necessary to consider transmission at a higher voltage. This introduces the alternating current generator and rotary converter combination of power supply. The relative location of power station and the pots or tanks where the current is used has, therefore, an important bearing on the choice of a power system. This will be referred to again in detail in discussing water power installations.

Voltage Variation.—Electrochemical plants usually require some means of adjustment of the voltage in order to maintain

constant current under the varying circuit conditions incident to operation. With direct current generators this is readily obtained by simple field-current control, a single generator usually supplying a single series of tanks. With rotary converters, if the required range is not more than 5 percent it can also be obtained by adjustment of the field current, assuming sufficient reactance to exist in the alternating circuit. If a greater range of voltage variation is required, several methods are available, the one commonly preferred at the present time involving the addition of a small alternating current generator to the rotary converter unit, this generator acting as a synchronous booster. In both generators and rotary converters, the performance under the wide range of voltage sometimes required has been greatly improved, in recent designs, by properly proportioned commutating poles.

Continuity of Service.—A feature of electrochemical load that has an important bearing on the satisfactory performance of the equipment is the requirement for steady full-load operation for long periods without shut-down. Many commutating machines that will operate with entire satisfaction on a fluctuating railway or lighting load will fail utterly on a continuous load of no greater value than the average load in the former case. The fluctuating load affords periods of light load during which the commutator and brushes can clean and polish themselves and the daily shut-downs permit the correction of incipient troubles. It is for this reason, more than any other, that serious trouble has been experienced in so many instances with commutating machines in electrochemical plants. For this reason alone commutating machines intended for operation in such plants should be of the most rugged and of the simplest type, and should be designed, particularly from the standpoint of the commutator, well within conservative limits.

The general problem having been stated, the various methods of meeting required conditions will be considered.

Steam Turbine Driven Units.—Four arrangements involving steam-turbine prime-movers have been more or less successfully operated:

(*a*) Direct-connected commutator-type direct-current generators.

(*b*) Direct-connected unipolar-type direct-current generators.

(*c*) Gear-connected commutator-type direct-current generators.

(*d*) Direct-connected alternating-current generator with rotary converter.

(*a*) Direct-connected direct-current turbo-generators are limited to relatively small current ratings, because of the very high speed necessary if reasonable turbine economy is to be obtained; and for such sizes as can be built suitable for electrochemical work, conservative design limits must be exceeded. For this reason it is almost impossible to build direct-connected units that will be generally satisfactory under the severe operating conditions inherent in electrochemical work. The efficiency of the direct-current turbo-generator is low, due to the high speed and frequency; that of the turbine is low, due to the speed, which while high from the standpoint of the generator, is low from the standpoint of best turbine performance. The trend of development, both in this country and in Europe, where the most work with direct-connected direct-current units has been done, is away from direct connected units.

(*b*) Since the difficulties in the design of direct current generators for electrochemical work have been mainly associated with the commutator, a generator from which commutation has been eliminated would seem to offer a way out of all troubles. In the unipolar type commutation is eliminated by the employment of unipolar flux, that is, flux of one polarity external to the armature. It is only necessary to collect the generated direct current from the two ends of the armature by means of collector rings and brushes, as commonly employed in alternating current generators and rotary converters. But it has required only two or three attempts with large units to show that with the increase in current and speed desired, the simple process of current collection becomes a more difficult problem than commutation at the lower speeds available with alternative methods. The only unipolar generator large enough to be considered for electrochemical power supply now in commercial operation is the 2,000 kw.-250 volt-8,000 ampere-1,200 r. p. m. unit described in a paper before the American Institute of Electrical Engineers.[1] This paper also

[1] Development of a Successful Direct-Current 2,000 Kw. Unipolar Generator, B. G. Lamme, June, 1912.

gives in detail the difficulties encountered and overcome before this unit could be operated with reasonable maintenance cost. Due to the low core loss and windage loss of this type, the efficiency is relatively high. The first cost and maintenance cost, however, are also high.

(*c*) With the development during the past three years of a satisfactory gear for the transmission of large powers, the direct production of large currents with steam turbine prime movers has been placed on a much more satisfactory footing. This gearing is usually of a double helical type with the pinion mounted in a floating frame so as to equalize the tooth pressures in spite of the long face necessary. Obviously, with an efficient and satisfactory gear available, the speeds of the turbine and the generator can be selected to suit the conflicting requirements of the prime mover and generator. As a matter of fact, generators which have been supplied for connection to turbines through gearing have been of the same speed and design as generators of the same rating driven by induction or synchronous motors in motor generator sets. For example, such ratings for 250 volts would be 1,000 kw. at 500 r. p. m.; 1,500 kw. at 360 r. p. m.; 2,000 kw. at 300 r. p. m., and 3,000 kw. at 180 r. p. m., which are all within the limiting ratings and speeds previously given. These units may, therefore, be designed as conservatively as similar generators used in motor generator sets with relatively high efficiency and low cost. Such units have been in service for several years and have amply proven their dependability. Two large units of 3,750 kw., the turbine operating at 1,800 r. p. m. and the generator at 180 r. p. m., have been supplied for lighting service.

(*d*) Another satisfactory means for obtaining the required direct current is afforded by turbine-driven alternating-current generators to which rotary converters are electrically connected. The alternating current generators may be of the usual synchronous type or of the induction type. This method has been used in a number of copper refining plants, and was used in industrial plants generally prior to the development of the geared unit. While it is lower in cost than either the direct connected or unipolar type of generators and higher in efficiency than the former, it is somewhat inferior to the gear-connected unit. This method

possesses obvious advantages in flexibility of plant arrangement. For plants in which the transmission distance is short enough, the generator can be designed for the required converter voltage and the converter connected directly to the generator terminals. Where, however, distances are greater, the generator can be wound for a higher voltage and step-down transformers installed with the converters at the electrolytic tanks.

Rotary converters have been used instead of motor-generator sets primarily because of their higher efficiency. Considering the most unfavorable conditions from the standpoint of the rotary converter, that is, a 60-cycle synchronous booster rotary converter with transformers, the efficiency of a 1,000 kw.-250 volt rotary converter outfit would be, at least, 92 percent, while the efficiency of an equivalent motor-generator set without transformers would rarely be higher than 88 percent. Without transformers, without the booster (where large variations in voltage are not required) and with a 25-cycle system, the comparison would be still more favorable to the rotary converter.

If it is necessary to entirely separate, electrically, the different circuits each consisting of a rotary converter and series of tanks, this can be done as effectively by the use of transformers in connection with the rotary converters as by the use of separate generators in motor-generator sets.

If transformers are necessary, the combined cost of the rotary converter and transformer will be substantially the same as that of the motor-generator set.

The inherent advantages of the induction type generator for this service have been pointed out in a paper before the American Institute of Electrical Engineers,[2] in which a specific application to electrolytic work was described. The stators of the synchronous and induction generators are substantially the same; the difference between them lies in the rotors. The rotor of the induction generator consists of a simple winding formed of bars short-circuited by end-rings, as in the more familiar induction motor. As in the motor, this winding need not be insulated from the core, and there are no collector rings and brushes, which, at turbine speeds, require some care and attention. While, however,

[2] The Non-synchronous Generator in Central Station and Other Work, W. L. Waters, February, 1908.

the induction type rotor is inherently simpler than the synchronous generator rotor, so much more development work has been done with the latter type that, as actually constructed, the synchronous rotor is, if anything, more reliable in operation than the rotor of the induction generator. The exciting or magnetizing current of the induction generator must be supplied from the rotary converter so that the rotary converter is under the handicap of operation at a power factor lower than unity. This handicap may become serious if it is desired to increase the voltage above that originally contemplated. The voltage of the synchronous generator on the other hand is very simply controlled by changes in its exciting current, so that in this respect the combined alternating current generator-rotary converter unit is on a par with the direct-current generator. For these reasons the induction generator has not been extensively applied.

The comparative efficiency of the various methods just described, based on a 2,000 kw.-250 volt unit, are given in the following table:

	Apparatus	Efficiency
(*a*)	Direct-connected commutator-type generator:	
	Three 750 kw.-1,500 r. p. m.	89
(*b*)	Direct-connected unipolar-type generator:	
	2,000 kw.-1,200 r. p. m.	92
(*c*)	Gear-connected generator:	
	Gear 3,600-300 r. p. m.	98
	Generator 2,000 kw.-300 r. p. m.	93.5
	Combined	91.6
(*d*)	Alternating-current generator-converter set:	
	A. C. generator, 2,000 kw.-3,600 r. p. m.	94.5
	Cables	99.5
	Rotary converter, 2,000 kw.-360 r. p. m.	96
	Combined	90.2

In considering these efficiencies, the lower economies of the lower speed turbines for (*a*) and (*b*) should not be lost sight of.

Water-Wheel Driven Units.—With water-wheel driven units, the choice lies between direct-connected direct-current generators or direct-connected alternating-current generators and rotary converters. In very few plants can water-wheel generators be located near enough to the electrochemical plant to justify the installation of direct-connected direct-current generators, in view of the expensive structure required for the transmission of the heavy currents. The various questions involved in such an instal-

lation can best be brought out by a comparison of the D. C. and A. C.–D. C. installations in a specific instance.

For this purpose a plant having an ultimate capacity of 120,000 h. p., with a water power having a 250 ft. head, has been chosen. The largest direct-current units that could be even considered are 5,000 kw.-250 volts, operating at a speed of 170 r. p. m. It will be noted that this current rating in proportion to the speed is higher than previously given as a conservative rating. Nineteen such units would be required, and with a diameter of approximately 25 ft. (7.5 m.) these generators would require a power house approximately 700 ft. (200 m.) long. Contrasted with the direct-current equipment, eight 12,500 k. v a.-277 r. p. m. 60 cycle generators could be used. These generators could be placed in a power house approximately 250 ft. (75 m.) long. In each case one spare unit is included. In further contrast with the direct-current units, the alternating-current units are well within conservative design limits, much larger generators at higher speeds having been built. With the direct-current units a lower speed has necessarily been chosen than would be most economical for the water-wheels, consequently the water-wheel efficiencies are lower for the direct-current plant than for the alternating-current plant. The comparative efficiencies with the two systems are shown in the following table:

	D. C. Generation	A. C. Generation and Rotaries
Water wheels	80 percent	89 percent
Generators	95 "	96 "
Transmission—assuming a distance of 2,000 feet	92 "	99.5 "
Stepdown transformers		98.6 "
Rotary converters		96 "
Low tension wiring from stepdown transformers to load (assuming 50 feet)		99.6 "
Overall efficiencies (from water to load)	69.7 "	80.1 "

Ten percent difference in efficiency would mean an appreciable difference in the investment cost and, therefore, in the cost of power even with a water-power installation. In the present instance, assuming an investment cost of $60.00 per h. p., this difference would amount to three-quarters of a million dollars.

The comparative costs of the two propositions based on the

total cost of the direct-current system as 100 are shown in the following table:

	D. C. Generation	A. C. Generation and Rotaries
Nineteen 5,000 kw.-170 r. p. m.-250 volt D. C. generators with water wheels complete (one unit a spare) approx.	60 percent	
Eight 12.750 kw.-277 r. p. m.-11,000 volt-60 cycle A. C. generators with water wheels complete one unit a spare approx.		38 percent
Transmission (based on 90,000 kw.-250 volt for 2,000 feet with copper, at 10½c. per pound, loss 8 percent) approx.	38 "	1 "
Nineteen 5,250 kw.-3-phase 60 cycles O. I. W. C. transformers, 11,000 to 180 volts (one unit a spare) approx.		4½ "
Nineteen 5,000 kw.-6-phase 250 volt D. C. rotary converters with 10 percent buck and 10 percent boost (one unit a spare) approx. (each unit consisting of two 2,500 kw. converters)		29 "
Low tension wiring from stepdown transformers to low (50 feet assumed) approx.		1 "
Switching equipment—approx.	2 "	7½ "
Totals	100	81

The above costs do not include the cost of supports, anchors and insulation for the direct-current transmission line which with the very heavy structure necessary would be a considerable item.

Obviously with a smaller plant and, particularly, with a shorter transmission distance, the cost of the direct-current plant would be materially less. The efficiency, however, would not be greatly improved unless more efficient wheels could be used and the drop in the transmission reduced by a material increase in the cost of this part of the plant. For example, for a plant of 60,000 h. p. instead of 120,000 h. p. and assuming 1,000 ft. (300 m.) length and 5 percent loss for the direct current transmission, the A. C.–D. C. plant would still have 8 percent higher efficiency, but its cost would be 10 percent more than the direct current. Even on this basis the A. C.–D. C. plant would be more economical. Its flexibility is, moreover, an additional advantage of great importance.

These figures are well substantiated by the change in practice found desirable by one of the largest aluminum companies. All of the recent work done by this company has been with alternating current generators and rotary converters. A large installation

involving nine 2,500 kw.-500 volt-60 cycle rotary converters is now being erected and a still larger installation involving 60 cycle machines of similar rating is in process of construction.

At the lower voltages more commonly involved in electrochemical work, a 60-cycle system has considerable advantage over a 25-cycle system. The higher frequency is an advantage from the standpoint of the turbine because of the higher available speeds; costs throughout the installation are less. In the rotary converters the higher frequency is an advantage due to the larger number of poles and armature circuits for a given speed. At the higher voltages, that is, 500 to 700, sometimes used for the reduction of aluminum, there is a slight advantage from the standpoint of the rotary converter design in the lower frequency. This, however, is not sufficient to overcome the other disadvantages incident to the lower frequency.

Reciprocating Engine Units.—While these units have very little application in modern plants, they should be mentioned to complete this survey. From the generator standpoint the lower speeds common with reciprocating units is a decided advantage, permitting as it does a large number of poles and armature circuits. On account of this fact there is no reason for considering other schemes than the simple direct-connected commutator-type direct-current generator. The efficiency of a 2,000 kw.-250 volt unit would be 94 percent.

Conclusion.—From the many schemes proposed for the generation of direct current for electrochemical plants, two plans assuming steam turbine prime movers have decided advantages in efficiency and reliability and flexibility in operation. These are the gear-driven commutator-type generator where the distance between the power plant and the place of utilization is short, and the combined alternating current generator and rotary converter plant when this distance becomes too great for economical low voltage transmission.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914, President E. F. Roeber in the Chair.

ELECTRIC FURNACE CURRENT REGULATORS.

By Robert Turnbull.

Present day business conditions, owing to the extreme competition to be found in every branch of trade, demand from the owner, manager and employees of all industries that every effort be put forward to keep down the cost of production.

The electric furnace today differs greatly from electric furnaces of ten years ago, the operating costs have been lowered by the use of larger furnaces, better methods of working same, automatic charging and stoking devices, the use of larger electrodes carrying greatly decreased current densities, and a host of other improvements all designed with the same end in view—greater economy of production.

One of the greatest improvements of all, however, and one which it is to be regretted has not yet been recognized by all users of electric furnaces, is the automatic regulation of the current. My object in taking part in this symposium today is to show the advantages to be obtained in the employment of automatic regulation for the control of the current operating the furnaces, and also the importance of using the Thury regulator for such control.

Before discussing this special type of regulator, let us first of all examine what benefits can be derived from the automatic regulation of the current, as compared with hand control. The following advantages of automatic regulation, as compared with hand control, may be obtained by the use of nearly all kinds of regulators:

1. A great saving in wages, in a three phase furnace, amounting to from 25 percent to 30 percent of the total labor employed on the furnace.

2. A more efficient utilization of the current, resulting in maximum production and shortening of the time of the process.

3. Products of a higher and more uniform quality, owing to the steadier furnace conditions.

4. The impossibility of mistakes, as the regulator always works in the proper direction, and never without due reason.

Besides these general advantages of nearly all kinds of furnace regulators, the following special advantages may be derived by using the Thury regulator:

1. The damping devices employed only permit the regulator to act, when it is necessary for it to do so. Sudden changes and changes of short duration will not put the regulator in action. This in itself is very important, as not only is there a great saving on the wear and tear of the electrode hoisting mechanism, motors for driving same, etc., but the current is kept more uniform by avoiding the regulation of such changes.

2. This regulator can handle any amount of power for regulating purposes without in any way impeding the free play of the controlling mechanism, which is only in contact with the power mechanism for exceedingly short periods of time and is otherwise perfectly free.

3. The regulator requires no attention whatever, and, with the exception of the oiling of the moving parts once a week, can be practically left to itself.

4. Great variations of current can be automatically obtained by the use of this regulator.

5. The intermittent action of the contact-making arm is important, as the regulation is thereby prevented from being carried too far in one direction, and a high load factor is assured at all times, and uniform current on the furnace.

The Thury regulator is the invention of Mr. R. Thury, of Geneva, Switzerland, the well-known electrician and exponent of direct-current long-distance transmission. His first regulator was designed to automatically regulate the magnetic field of dynamos, and consisted of a relay with platinum contacts, by which the current was transmitted to either of the two electromagnets, which in turn put in motion the arm of the rheostat, by the intermediary of friction cones. This regulator, although crude in construction, was used successfully for some years by the Allgemeine Elektrizitäts Gesellschaft of Berlin, who bought

the license for its manufacture. Mr. Thury, being far from satisfied with his contact relay, which he found in practice to have many inconveniences, began a new study of the question, and the result was the production of his Tappet regulator, an apparatus now universally known. Patents for this type of regulator were taken out in 1898. The introduction of the tappet device is not the principal innovation in the Thury regulator, as this

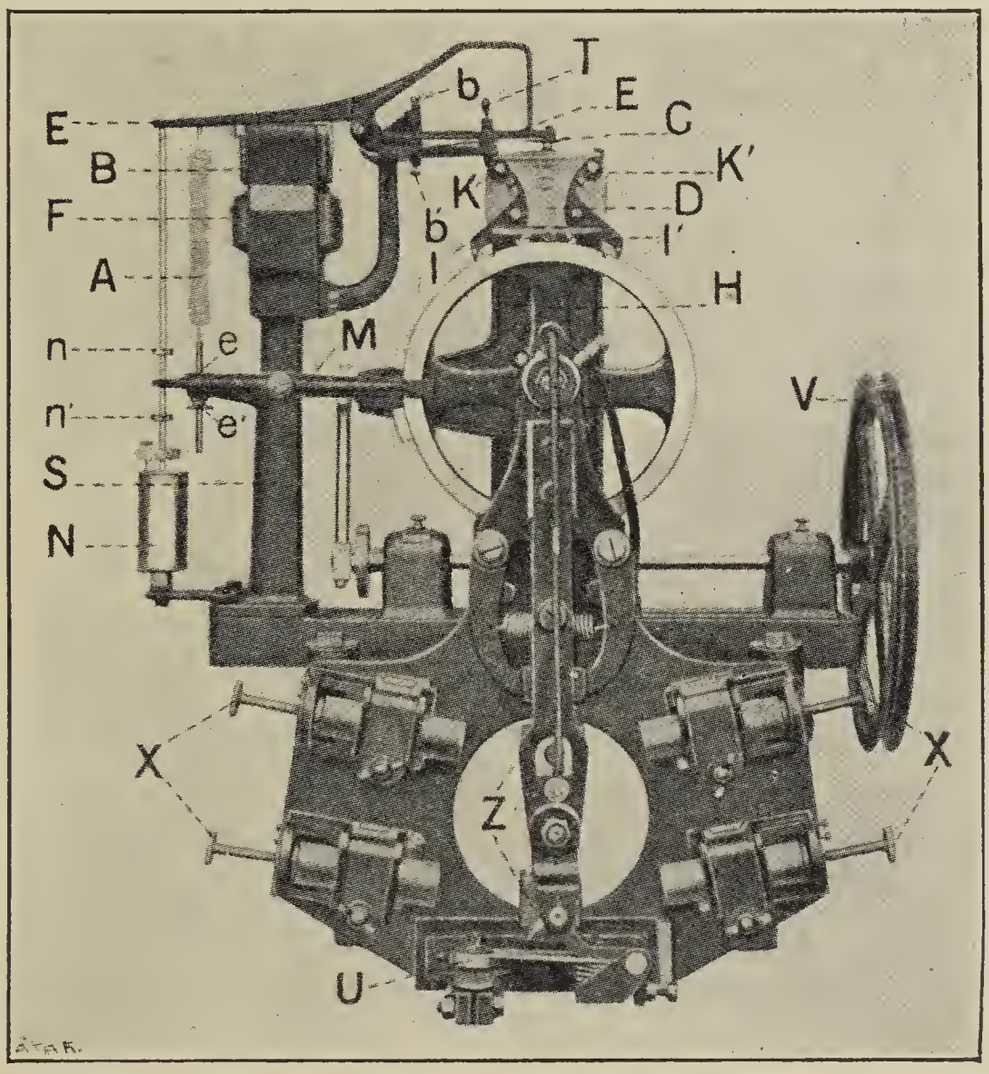


FIG. 1.

same device had already been employed by Mr. Piccard, of Piccard, Pictet & Co., of Geneva, in the regulation of their turbines, but Mr. Thury was able, by means of a very ingenious arrangement, to put the tappets in action by a relay without contacts, and he added to the apparatus the damping device, which permits the control of the current within very narrow limits.

The first application of this type of regulator to electric furnaces was made in the year 1901, to the first steel furnace designed by Dr. P. Héroult, at the La Praz works of the Société Electrometallurgique Française, and, if I am not mistaken, this same regulator is still in action at the present day.

I will now endeavor to give a short description of the Thury regulator, and in order to make it more intelligible will show some illustrations. The principal parts of the regulator (Fig. 1) are as follows:

1. The Fixed Coil *F*.
2. The Movable Coil *B*.
3. The Rocking Lever *E*.
4. The Spiral Spring *A*.
5. The Dashpot or Damping Device *N*.
6. The Abutment Knives *C*.
7. The Tappets *K*.
8. The Pawls *I*.
9. The Tappet Wheel *H*.
10. The Copper Contacts *Z*.
11. The Carbon Contacts.
12. The Short-Circuiting Device *U*.

The regulator operates as follows:

When the current operating the furnace is at its normal value, the rocking lever *E* is held in equilibrium by the pull of the spring *A*, and the magnetic force of the fixed coil *F* acting on the movable coil *B*. The knives fixed to the rocking lever in this position swing clear of the tappets *K*. When a variation of sufficient duration occurs on the furnace, the movable coil will either be pulled to or pushed away from the fixed coil, depending on whether the current has decreased or increased on the furnace, and the rocking lever will swing either the one or the other of the knives against one of the tappets *K*. The tappet is pushed from its position, releases the pawl *I*, which falls into the notch in the tappet wheel. The arm carrying the copper contacts, which is fixed to the tappet wheel shaft, will then swing either to the right or to the left, bringing the copper contacts against the carbons, and current will immediately flow to the terminals of the winch motor.

The Cuenod Company of Geneva, Switzerland, which now controls the manufacture of the Thury regulator, has added to the regulator a series of apparatus, which taken together form

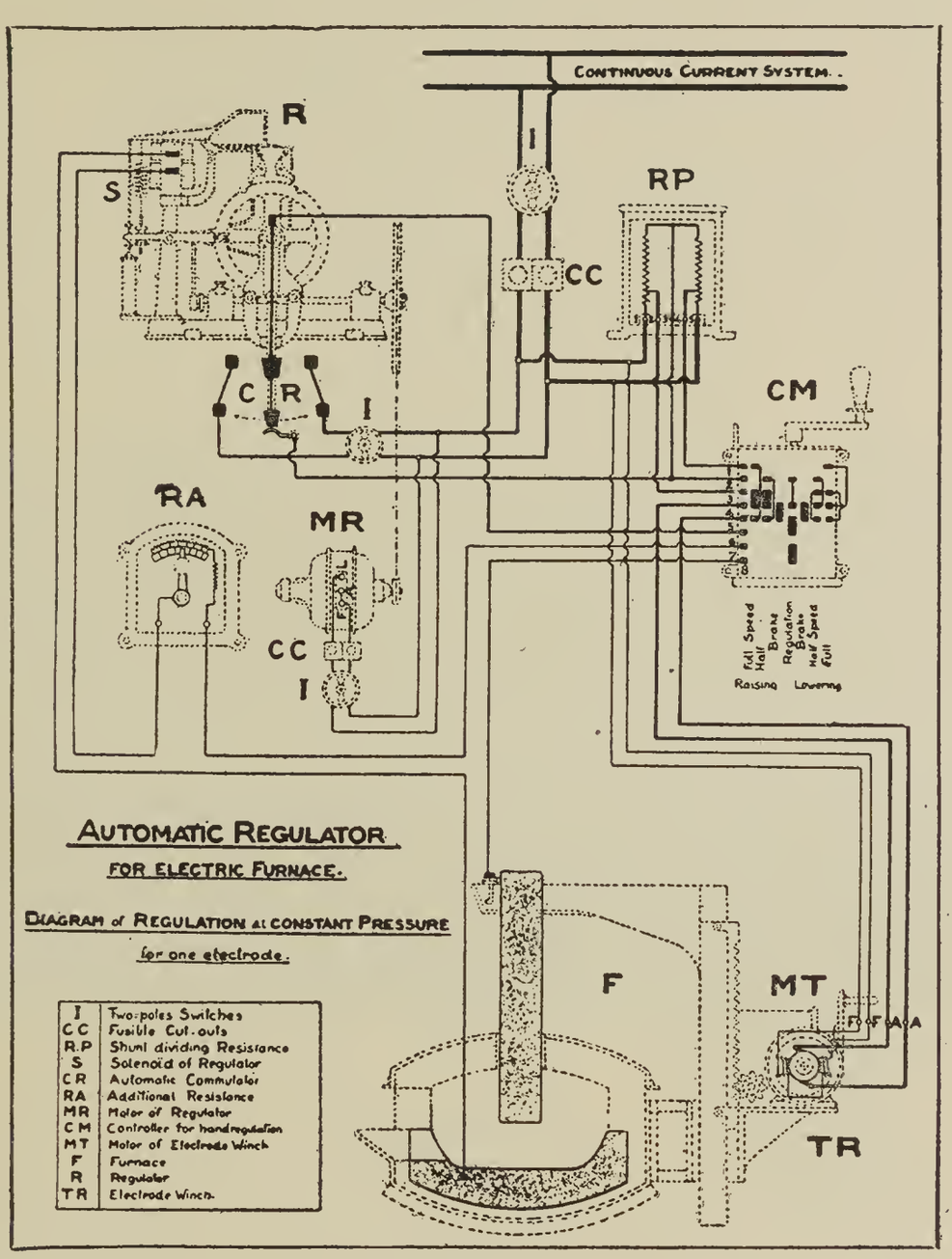


FIG. 2.

a very complete regulator system. This system can best be described by reference to Figs. 2 and 3.

It consists of the following:

1. A winch *TR* for raising and lowering the electrodes.

2. A double-throw switch with carbon contacts *CR*, worked by an automatic Thury regulator *R*, which starts, stops and reverses the motor *MT* as desired.

3. An adjustable resistance *RA*, permitting a modification of the current on the furnace, for instance, from 2,000 to 10,000 amperes, by steps of 1,000 amperes.

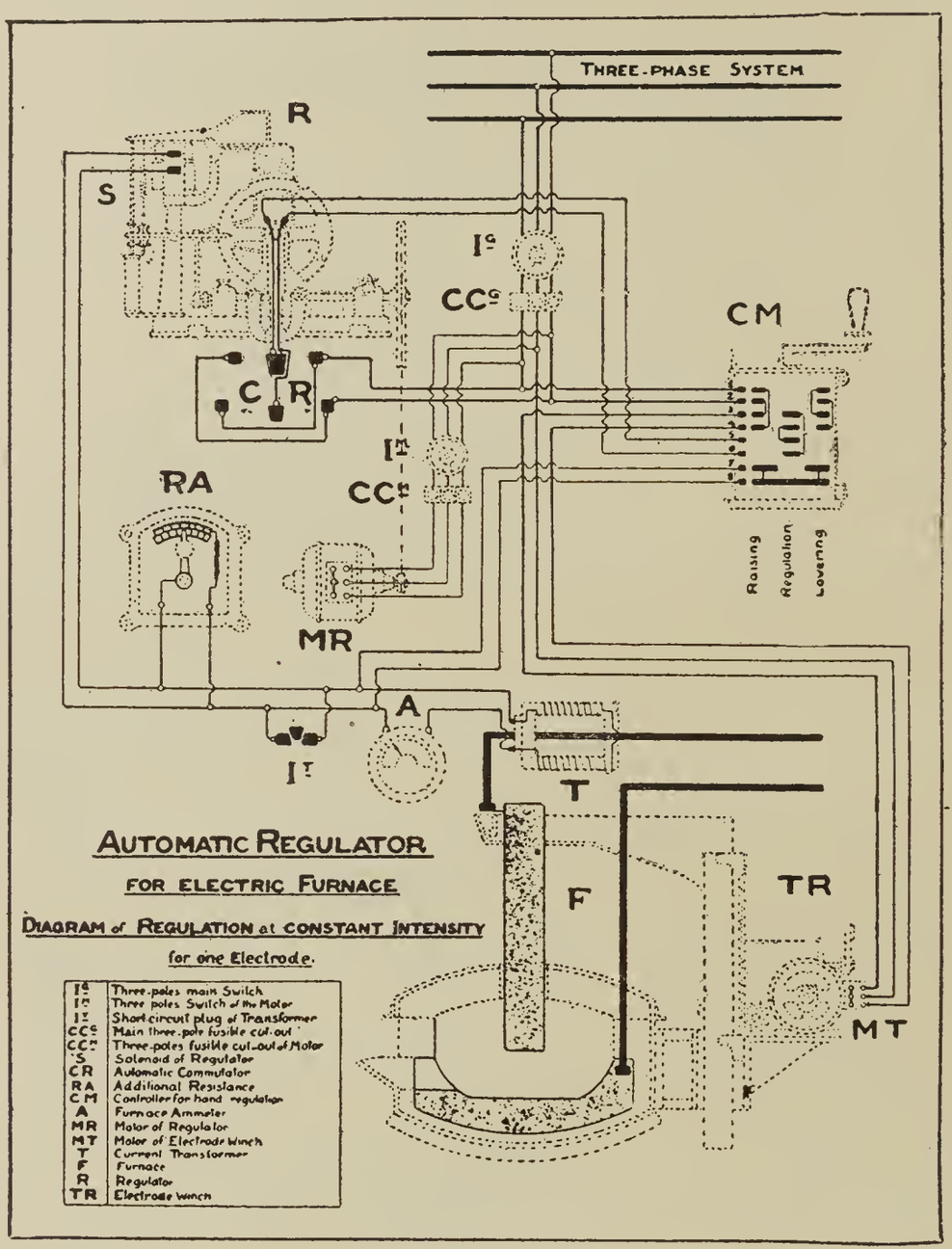


FIG. 3.

4. A controller *CM* for hand and automatic control.

5. A current transformer *T*, operating the solenoid of the regulator.

One cycle of operation in this system would be as follows:

We will suppose that the current flowing through the secondary bars to the furnace is above the normal. The current flowing from the secondaries of the transformer *T* to the solenoid of the

regulator, will also be above normal, and the increased magnetic force will push the movable coil against the pull of the spring until the knife *C* will encounter the tappet *K*, pushing this latter out of position, thereby releasing the pawl *I*. This pawl falls into the notch in the tappet wheel *H*, which in turn brings the copper contacts *Z* on the lever in contact with the carbon contacts, and the current immediately flows to the winch motor through the controller *CM*. When the current on the furnace has been brought back to its normal value, the regulator will cease to act and the lever carrying the copper contacts will remain in its central position, until again called upon to act, through a variation of current in the furnace.

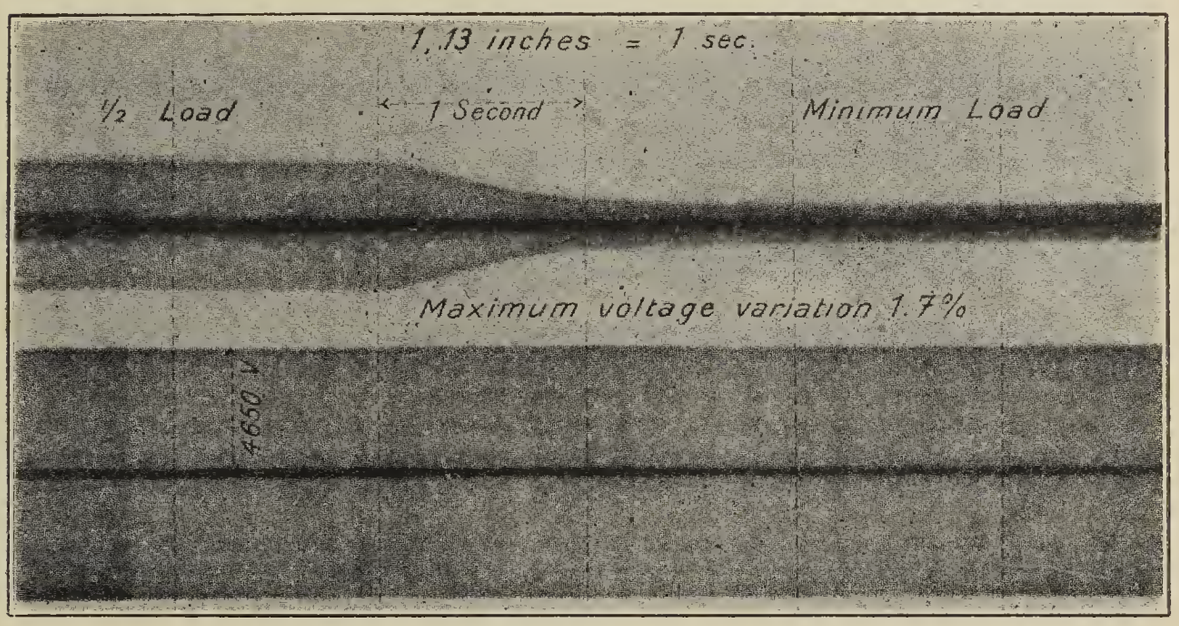


FIG. 4.

I do not happen to have any charts showing the difference between hand and automatic control in electric furnace work. Good results have been obtained in the regulation of the pressure in a generating station at Marseilles, France, and similar results are possible in electric furnace work.

A special feature worth noting was that increased pressure was obtained automatically by the regulator, during the peak load hours from 5 P. M. to 8 P. M., the voltage being maintained constant at the lamps during this period.

For the benefit of those members who are not especially interested in electric furnace work, but to whom the regulation of

the voltage, in generating and distributing stations may appeal, I will conclude by showing in Figs. 4 to 7 what can be accomplished by the Thury high-speed regulator in this direction.

Figs. 4 to 7 are oscillograph curves, taken during a series of tests made by the Oerlikon Works of Zurich, Switzerland, in order to determine the effectiveness of this apparatus for special conditions.

In these tests the machine whose voltage was to be maintained constant was a 1,300-kw., three-phase, 50-cycle turbo-generator with the exiter on the end of the shaft.

The load was obtained by a synchronous motor running light, the field current of which was varied to give the required full-

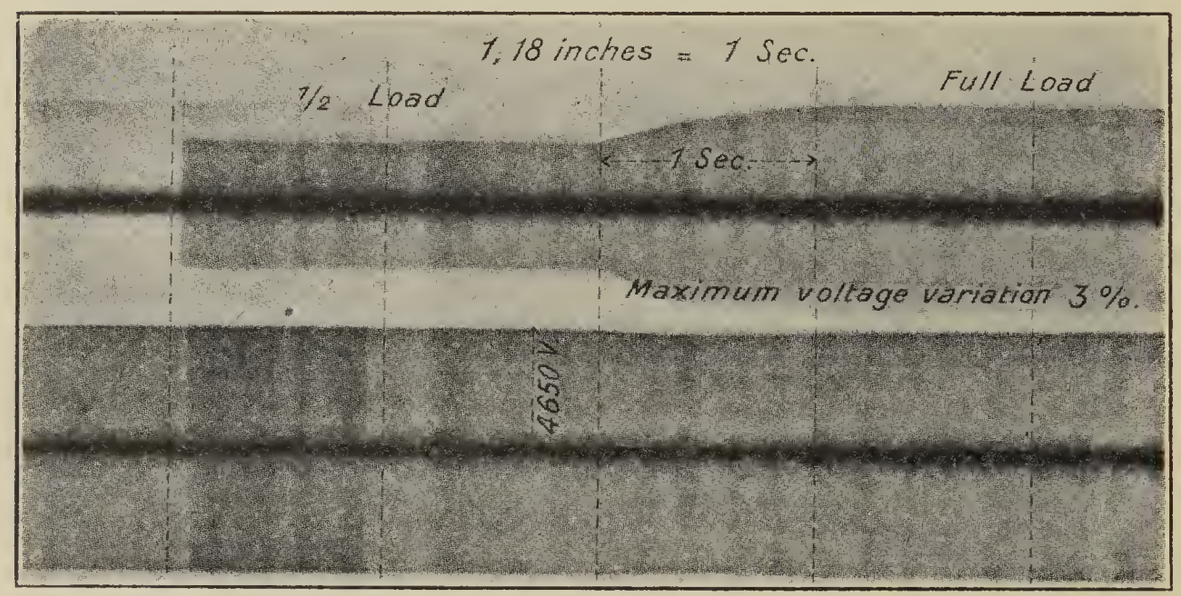


FIG. 5.

load amperes. As the power factor was practically zero, the drop in voltage of the alternator was maximum, this drop from no load to full load being 25 percent.

The regulator operated by increasing or decreasing the resistance in series with the field circuit of the alternator, the exciting current varying from 70 to 150 amperes, the quadrant having 40 contacts.

The results obtained are shown by means of the oscillograph curves, Figs. 4 to 7. The drum of the oscillograph was operated very slowly, the sine waves being indicated almost in vertical lines, symmetrical with regard to the axis.

Fig. 4 shows the effect of decreasing the load from half load to minimum load by operating quickly the field rheostat of the synchronous motor. It will be noticed that the voltage variation is almost negligible and after less than one second the voltage was normal again.

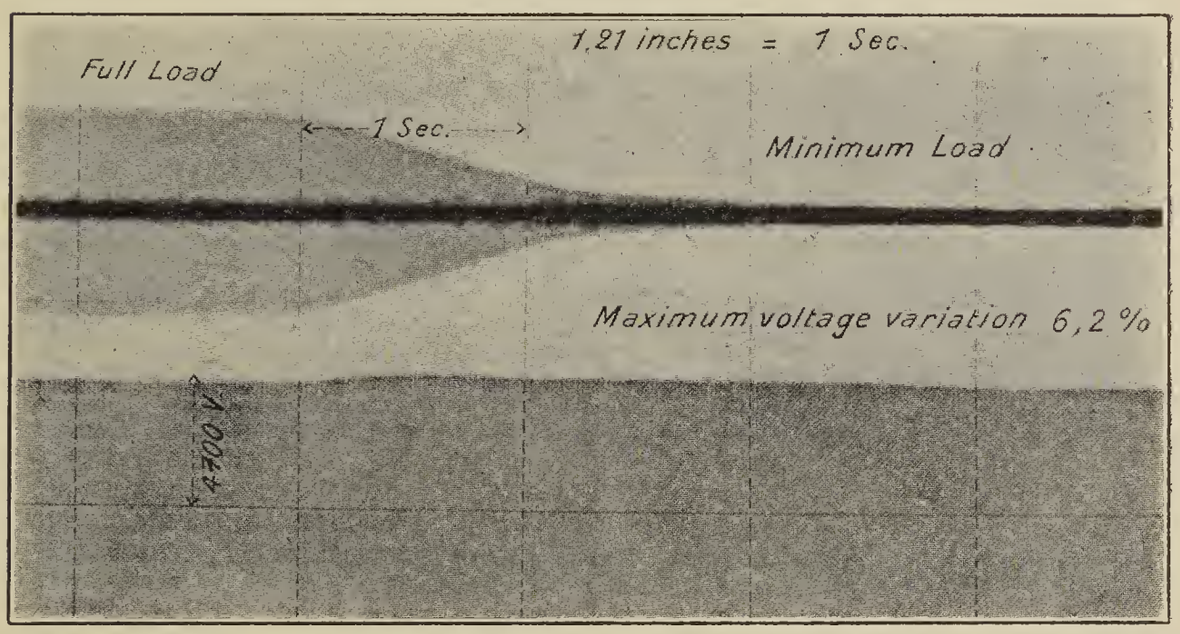


FIG. 6.

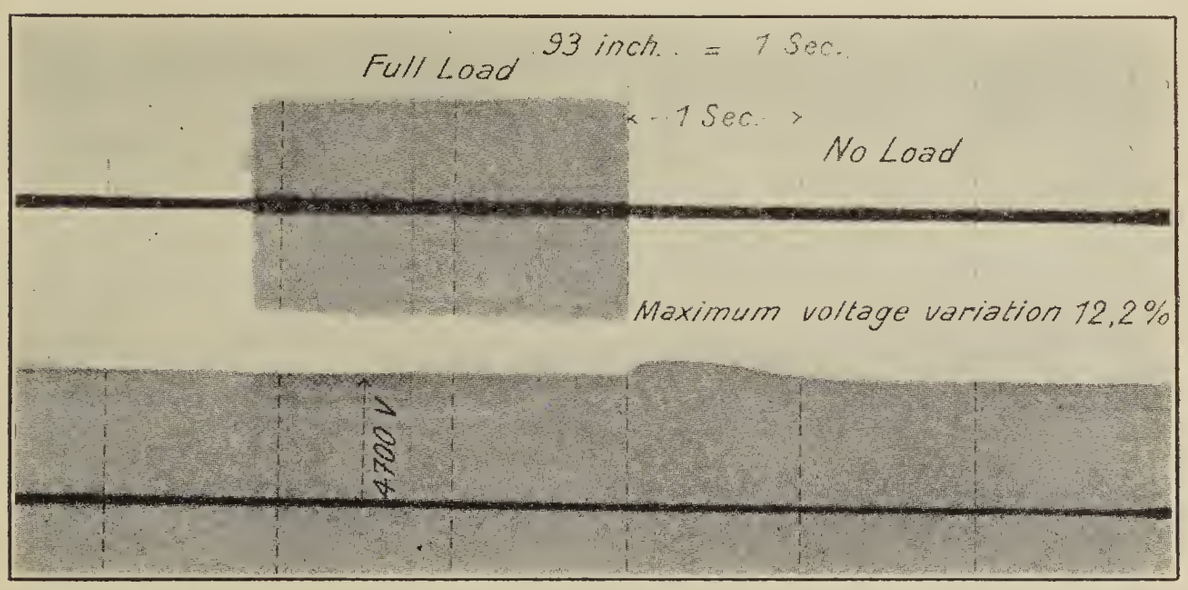


FIG. 7.

Fig. 5 shows the effect of increasing the load from half load to full load by operating quickly the field rheostat of the synchronous motor. The time necessary to restore voltage to normal was approximately one second.

Fig. 6 shows the effect of decreasing the load from full load to minimum load by operating suddenly the field rheostat of the synchronous motor. The regulator took approximately two seconds to restore the voltage to normal, but it will be noticed that at the end of 1.5 seconds the voltage was practically normal.

Fig. 7 shows the effect of decreasing instantaneously the load from full load to no load by opening the oil switches. The time required to restore voltage to normal was one second.

GENERAL DISCUSSION ON THE SYMPOSIUM.

ROBERT TURNBULL: Some of the papers presented in this symposium have touched on the question of off-peak power, and no doubt there are some members present who are producers of power. I have lately been trying to buy some off-peak power, but find there is such a difference in the ideas of price on this question that it is hard to decide what to do. One feels inclined to wait until one gets the lowest figure. If I am not asking too much, I would like to ask some gentleman what he would consider would be a fair price for off-peak power. People who are making a study of the electric furnace understand that off-peak power is a pretty hard thing to handle in electric furnace practice, as Mr. FitzGerald has told us, and it would be interesting to know what one would have to pay for this class of power.

N. PETINOT: Referring to Mr. Turnbull's paper on the Thury automatic furnace regulator, I would like to say that the Titanium Alloy Manufacturing Company, of Niagara Falls, use this type of regulator in connection with the furnaces in the production of ferro-titanium. The regulator is as nearly perfect as one could wish with automatic regulation, whereas regulation by hand in the manufacture of this alloy is almost impossible, owing to the extreme variations of current on the furnace. The load factor can be kept as high as 97 or 98 percent by the use of these regulators. I have also seen the Thury regulator used in connection with the manufacture of ferro-silicon and calcium carbide, and as the furnace conditions in these products are better and steadier than in the manufacture of ferro-titanium, a load factor approaching very near 100 percent is attained.

I have also had some experience with various automatic regulators in the operation of electric steel furnaces, and consider the Thury is the most reliable for this purpose. I do not think it would be too much to say that the Thury regulator has been one of the essential features which has brought electric steel furnaces of the Héroult and Girod type to their present-day perfection.

C. A. HANSEN: Dr. Steinmetz spoke of the advisability of running furnaces and electrochemical processes generally at relatively low power factor—or at least of not trying for 100 percent power factor.

I do not believe that there is great danger of too closely approaching unity power factor in many cases even with a design eliminating as much reactance as we can.

Wave distortion does enter to materially affect power factor in some cases with which I am familiar. The following characteristics of a ferro-silicon furnace operating single phase at 60 volts and 40 cycles may be of interest. Here measurements are referred to primary voltage. Actual phase displacement was measured by oscillographic means and true reactance ohms calculated. Apparent reactance ohms were calculated from wattmeter, ammeter and voltmeter readings:

Amps.	Volts.	KVA	KW	PF	Apparent Reactance Ohms
22.80	10,320	235	228	97.2	105.5
31.32	10,320	322	309	96.2	90.0
44.00	10,420	458	406	90.8	99.0
64.32	10,280	661	573	86.8	79.0
89.20	10,210	911	739	81.2	67.0
100.75	10,150	1022	796	78.0	63.5

Amps.	Volts	KW	ϕ	Cos. ϕ	Reactance Ohms
26.0	10,400	260	7°–48′	99.07%	54.2
35.0	10,500	330	10°–12′	98.43%	53.2
65.5	10,300	583	24°– 0′	91.35%	63.8
73.0	10,200	630	26°–42′	89.30%	62.8
101.0	10,300	800	38°–54′	77.85%	63.9
118.0	10,100	870	41°–31′	74.89%	56.8
					Av. 59.1

The difference between true and apparent reactance ohms shows what part was played by wave distortion, and the latter was not at all bad in this case. The voltage wave was practically a true sine.

A more complex instance of this same wave distortion is to be found in all arc type steel furnaces. In the case of a two-ton, three-phase arc furnace operating at 90 volts and 40 cycles, the actual phase displacement at 300 kw. load is almost negligible. The power factor increases with increasing load—the wave distortion diminishing with increasing current. Finally the reactance voltage becomes appreciable and the wave distortion inappre-

ciable, and the power factor falls off with further increase of current. The following data, in this connection, may be of interest. Here one phase only was metered—potentials being taken between secondary terminal of transformer and the neutral. The load was a balanced three-phase, and total load may be taken as three times the power given in the table:

Current	Voltage	KVA	KW	PF	Apparent Reactance Ohms
950	50.5	48.0	45.1	93.90%	.0183
1380	48.5	66.9	63.3	94.60%	.0114
2000	47.7	95.5	93.1	97.58%	.0052
2500	51.3	128.2	123.6	96.40%	.0055
3040	51.5	156.5	150.4	96.02%	.0057

Very pretty triple harmonic potential graphs may be obtained between the ungrounded molten metal bath and a true neutral when the furnace is operated on a three-phase delta. On unbalanced load a very considerable direct current voltage may be measured between these two points. This is, of course, due to the well-known behavior of arcs between dissimilar electrodes—in this case carbon and slag. Wave distortion is very much more marked when the slag is practically free from FeO than when the usual oxidizing slag is used.

Neither of the above cases are at all serious, inasmuch as at normal load, wave distortion is not great.

Oscillograms have, however, been published, showing the wave distortion in connection with the atmospheric nitrogen fixation furnaces. The current waves here take very fantastic forms, and power factor as a function of wave distortion must be a very much more serious matter than mere reactance.

I may also say that I have seen a 50,000-amp., 25-volt installation go in where little attention was paid to reactance—on Dr. Steinmetz's principle that a little reactance would help on short circuit. The short circuit current on the above installation was 23,000 amps.—that is, without the furnace in circuit. It is rather obvious that the furnace fared but poorly.

F. A. Lidbury: Consideration of the power problem in electrochemical industries is beset with an extraordinary complexity of different considerations, different factors to be taken into account; and it has been rather instructive to observe that each of the speakers, while dealing with one specific phase

of the subject, has shown how complicated the matter usually is, even when dealt with from one point of view only.

Mr. Sothman did not exaggerate the importance of the question under discussion. He gave figures showing horse-power per employee in various classes of industry, and stated that he was not aware of the corresponding figures in electrochemical and electrometallurgical lines. They begin about where the figures he gave left off, *viz.*, at about 20 h. p. per employee, and range upwards from this figure to over 100 h. p. per employee—I would not be willing to make a guess at what the upper limit now is, and, still less, as to what it may be in the future. This will suffice, however, to show the importance of the power item as compared with the labor item in a number of cases. But there are considerations that are sometimes of more importance than power, and of these the question of geographical location is perhaps the greatest. Questions of proximity to raw materials and market have to be considered, not separately, but in connection with the question of power supply. I very much regret that Mr. A. H. Hooker, who has given very close attention to this phase of the subject, has been prevented from carrying out his intention of attending this Symposium and contributing some remarks along this line; and I shall attempt to induce him to contribute these remarks later. It must be clear, however, that the power question is one which can only be satisfactorily discussed in relation to any particular case when all such factors are known and taken into consideration; and, while such a discussion as today's is of extreme importance as calling attention to a number of points frequently overlooked, it should be borne in mind that it is a very dangerous subject to generalize on, having regard for the very varied nature of electrochemical and electrometallurgical industries. What may be excellent and logical practice in one case may be extremely bad in another; and it was from this point of view that I called attention, in the New York Section Symposium, to the fact that Mr. Newbury had discussed the question of direct current generation from water-power from a point of view of an installation of a magnitude not yet realized and only conceivable in one branch of the electrolytic industry. It is so often the case that smaller concerns blindly follow what they observe to be the current practice of

large concerns, without pausing to consider the problem carefully from the point of view of their own conditions, that it seemed desirable that it should be pointed out that Mr. Newbury's conclusions in this respect would not apply to the vast majority of electrolytic installations.

It must not be forgotten also in discussing any phase of this subject that the electrochemist looks at these matters, and rightly so, from a somewhat different point of view from that of the electrical engineer. The electrochemist has an absurd prejudice in favor of simplicity, and sometimes shows an unaccountable willingness to pay for it. But there are good reasons for this. In the first place he has sometimes had reason to doubt whether the over-all efficiency under operating conditions of a complex chain of electrical apparatus is fairly represented by the product of the efficiencies under test conditions of the individual links in that chain; and in the second place experience may have taught him that reliability and ease of operation are not necessarily most easily obtained by multiplying the links in his electrical chain. He has enough worries of his own without desiring to add to them those of the Central Station Superintendent and he does not wish to be placed in the position in which the proprietor of an extensive but somewhat primitively run business found himself after installing a modern business system. A year after its installation, the expert who installed it came to inquire how it was running. "Perfectly," was the answer. "I never saw anything run more smoothly in my life." "I am glad to hear it," said the salesman, "and how is business?" "Oh.... we haven't time to do any business!"

C. P. Steinmetz: Wave shape distortion has been studied very thoroughly in the study of the electric arc. It was first observed about twenty years ago in the series arc lighting system, and naturally the effect of reactance in wave shape distortion was then observed. The wave shape distortion we find in the electric furnace is essentially the same as met with in the electric arc, and while to the electrochemist at first it appears rather mysterious, all these phenomena are known to the few who have gone into the study of the wave shape distortion. The best that can be said of the most desirable form of wave shape

distortion in the electric furnace is to get rid of it as much as possible.

The most important factor in reducing wave shape distortion is reactance. If you lower the power factor by reactance you lower the wave shape distortion and thereby eliminate the reduction of power factor due to it. That means that where attempts are made to get as high power factor as possible by cutting down all the reactance in the furnace, the results have very often been disappointing.

I know of one case, for instance, where some time ago an electric furnace operated very satisfactorily at about 80 percent power factor by the use of reactance, but that was too low power factor for the electrochemist; he wanted to get good power factor and eliminated the reactance. With no reactance the power factor was no better, because there was now wave shape distortion, and, incidentally, the constancy of power operations was naturally very greatly reduced. The maximum peak greatly exceeded the average load, which meant higher cost of power, and incidentally there came electrical troubles inherently due to the sudden changes of current at the low power factor, and further experimentation was stopped by the receiver.

In my opinion, the greatest mistake in most furnace operation is the attempt to get low reactance. I do not believe it is good practice to attempt to operate at less than 80 to 85 percent power factor as calculated by the reactance resistance. Furthermore, there is a reduction in the excess power charge which the operating company has to make in limiting the maximum demand, if the maximum peak is lowered by sufficient reactance. You must realize that in the difference between 80 per cent and 60 percent power factor, the total variation of power is only 2 percent, while current and voltage vary about 30 percent. After all, in the electric furnace, the current and voltage are of secondary importance, and the matters of importance are the power, the temperature, and whether you can get constancy of power—it does not matter whether the voltage or current varies in general—the important feature is constant power consumption and high reactance gives you that, and I believe that we should have, in electric furnace operation, a power factor not much

exceeding 80 percent, and at such a value the wave shape distortion is small.

If you want unity power factor in your furnace, a much more economical way to get this is by synchronous condensers, synchronous motors with over-excited field. Also, where the power factor is limited, where you have to pay for power you do not get if the power factor goes below 90 percent, we must realize that 90 percent power factor means 44 percent inductance factor. With 90 percent from leading to lagging current, your reactive volt amperes can vary from 44 percent one way to 44 percent the other, 88 percent,—a very considerable range.

Practically the same thing is true in the case of phase balance. Synchronous condensers can be made to balance phase very easily, without complication; but all these limitations, it must not be forgotten, are not so formidable, if you use high enough reactance and keep the furnace simple. You must not attempt to run the furnace at constant voltage and at unity power factor. An electric furnace is bad enough in itself without unnecessarily creating bad electrical characteristics. If you get the furnace going at constant power and take care of the supply demands, by the synchronous condensers idle on the system, you will find in general the best operation.

As regards the question of the triple harmonic, that also is a well known characteristic of the voltage between the neutral and the phases of the three phase system, and has to be studied. It may give serious trouble if you connect the neutral of the transformer to the neutral of the furnace.

P. M. Lincoln: I would say just a word about the matter of power factor touched upon by Mr. Hansen. He put certain figures on the board and spoke of the true power factor and the power factor as derived by the oscillograph. The power factor meter does not always give true power factor; it gives only one thing, and that is the phase angle between the fundamental of voltage and the current. That is all that a power factor meter can recognize. If the current wave is of the same shape as the voltage wave, the power factor meter gives true power factor, but if the current wave and the voltage wave are not of the same shape, the power factor meter does not give

the true power factor, and the true power factor must be determined in some other way. Whenever we have an arc present the current wave is usually not the same as the voltage wave. The arc induces electromotive force in the circuit, so that the current wave departs very considerably from the voltage wave that produces that current. Consequently, when we have an arc present in the circuit the current wave will usually not be of the same shape as the voltage wave, and, therefore, the indications of the power factor meter cannot be entirely relied upon.

Just a word as to some of the power cost papers. Mr. Horry in his paper referred to the paper presented before the American Institute of Electrical Engineers by Mr. H. M. Hobart on power costs. I want to call attention to the fact that the paper by Mr. Hobart gives the cost of power for the very best conditions that can exist at the present time, for the very largest amount of power and the very highest load factor. If any of you are willing to offer a contract to a power company for the matter of, say, 50,000 kilowatts, and care to guarantee the load factor at 100 percent,—that is, twenty-four hour power, three hundred and sixty-five days a year,—and are willing to guarantee that that load shall remain on that power house for the next twenty years, I think that, these conditions assured and guaranteed, you might be able to get the cost of power somewhere in the neighborhood of the figures given by Mr. Hobart, but not if these conditions must be departed from. If you cannot guarantee the load for twenty years, it is a question whether it would pay the power company to enter into the large first cost which would be involved.

I just want to call your attention to that point, because I do not want some of you to be disappointed when you go out to buy power for some of your processes and find you cannot approach anything like Mr. Hobart's figures. The reason you cannot approach them will be because you cannot guarantee the conditions necessary to produce the figures stated by Mr. Hobart.

One word more, and that is in reference to Mr. Newbury's paper. With every one of the points in Mr. Newbury's paper I must express my agreement, and take exception to those gentlemen who cannot agree with them.

Now, the points presented in Mr. Newbury's paper, the crux

of the matter, relate to the modern conditions, especially the steam turbine, which is the most efficient and cheapest, and in general, the best method of getting mechanical power from steam. Unfortunately, the steam turbine is inherently operated at relatively high speed. On the other hand, the direct-current generator—and Mr. Newbury's paper refers to the obtaining of direct-current power—inherently cannot be run at the high speed necessary with steam turbines. That being true, we have to adopt some other method of getting the direct current power from the steam turbine. There are two methods of doing this. One of them is to use the gear, and that works out very satisfactorily in many cases. The other method is to use an alternating current generator which can be readily adapted to the higher speeds and then obtain the direct current by rotary converters or something of that nature, rotary converters being by far the most efficient scheme to use.

It is the necessity, therefore, of using the steam turbine in order to get the high economies and low costs of turning thermal energy into mechanical energy, and the impossibility of getting direct conversion from these high speeds into direct current, that makes the method outlined by Mr. Newbury the desirable one. I believe further analysis will show that there can be no question but what the method outlined in Mr. Newbury's paper for obtaining these results is the best one.

E. F. Roeber: It has been very interesting to hear from Mr. Lincoln, the President-Elect of the American Institute of Electrical Engineers, but that reminds me that not one of the distinguished Electrical Engineers who are here today has answered Mr. Turnbull's first question as to the reasonable cost of what is called "off-peak power." It would be very interesting to the electrochemists to get at least an estimate as to what that cost is.

P. W. Sothman: While I was connected with a large and important enterprise in Canada, I made numerous contracts for so-called "off-peak power." Mr. Lincoln very rightly emphasizes the importance of certain items which enter into such contracts and which have a very great bearing on the real cost of power. If I am told merely that the cost of power is $10.00,

I am at a loss to understand what is meant thereby. One of the most important points in power contracts is to formulate in what manner power is to be measured and what provisions are inserted in the contract affecting its original meaning.

In connection with this question, I wish to cite a few instances where contracts with power customers were made, illustrating the difficulties encountered. For instance, a contract might read as follows: You will get power at $28.50 provided the power is used twenty-four hours a day three hundred and sixty-five days in the year. However, if you elect to waive 80 percent of your power supply during the one and one-half hours of peak load period in the four months of November, December, January and February, the cost of power to you will be $24.00, equivalent to a reduction in your bill of 15.82 per cent. In certain other contracts which I had occasion to make, this reduction was as much as 24 or 25 percent for this off-peak power.

In the electrochemical industries, especially in the steel industry, I find that there is a big field for the utilization of off-peak power. I believe we all agree that the question of power is one of the greatest importance in the electrochemical industries. If an electrochemical process can be suspended or interrupted without injurious effects for a certain definite time every day, known in advance, it would be well to buy off-peak power, as the cost of power as compared to labor is a large factor in the total cost of production. Which figure would prevail, the cost of power, or the wages of employees, must naturally be determined in each particular case. The cost of labor enters into the question of total cost because the cost of labor figures against the cost of power. For instance, if ten men are working on a certain process which requires energy to the amount of 1,000 H. P. and off-peak power can be obtained 25 percent cheaper, a little calculation will show that it would be more economical to suspend the operations of these ten men for an hour or an hour and a half and get the total power used at the reduced value, always assuming, of course, that the process will not suffer from such an interruption and the final result of the work will be the same.

It cannot be too strongly emphasized that wherever a power contract is made, the individual responsible for the same must

keep his eyes wide open in order to eliminate clauses which, from both the consumer's as well as the producer's point of view, are not entirely free from objection.

ROBERT TURNBULL: I am very glad my question has been answered to some extent. In Niagara Falls we open our eyes very wide, but there is one point I would bring up, which was not mentioned by Mr. Sothman. It is not only the question of labor which is the main feature involved in this proposition, it is the question of a furnace being shut down. Furnaces engaged in electrochemical processes cannot be shut down without great loss in efficiency. In the case of a ferro-silicon furnace a one-hour shutdown means two hours to get it back to where it was before the shutdown—it takes from two to six hours to get back again, depending on the duration of the shutdown. Running on an eighteen-hour day basis, a ferro-silicon furnace would produce about the same amount as a furnace running twelve hours on a twenty-four hour basis. We really would lose six hours during that time, which would mean that the off-peak power would have to be sold at a much greater reduction in price than Mr. Sothman mentioned.

I think the main point in the whole thing is a question of getting some kind of a process which will permit of a furnace being temporarily shut down, without taking so much time to get back to its efficiency again. I think such a solution, coupled with off-peak power at a reasonable figure, would open up a wide field for this class of power.

CARL HERING: Referring to Dr. Steinmetz's very clear presentation of the subject of power, I wish that the managers of power stations would read it with thought, because it seems to be difficult to convince them that it is to their own interest to create loads by selling valley power quite cheaply. Their general rule seems to be to charge all that the traffic will bear.

Dr. Steinmetz recalled the statement that the transportation of coal on a railroad is in fact one way of transmitting power, or energy as he very correctly called it. In such a comparison, however, it is not the cost to the railroads of carrying the coal, which is the real determining factor, but the price which they charge for transporting it. If they charge for transportation

more than the value of the coal, as they do in many cases, the real efficiency of that form of transmission is less than 50 per-cent.

Dr. Steinmetz has very correctly pointed out the impracticability, or, in fact, the impossibility of storing electrical energy in large quantities in storage batteries, which, of course, is quite true. There is, however, an indirect form of storage which he did not mention directly, which is possible in connection with electrochemical industries, namely by the storage of the products produced. That is sometimes a very effective and practicable way. In such cases, even if the plant must be shut down for say three months in the year, if during the other nine months one can produce as much product as one can sell in a year, one has, in effect, stored the energy for those three months.

Mr. Hansen called attention to the deception of the innocent public which is practiced by some, and he illustrated it by citing the case of the transforming of three-phase current into single-phase current. I heartily agree with him, and think we should all join in exposing those who misrepresent things to the public. There is a still worse method, which I have heard advocated by some, and that is to get the single-phase current directly from three-phase current by some cross connections. On the other hand, if three-phase current is converted into single-phase by means of a motor generator, in which there is a fly-wheel effect for the momentary storage of energy, there would not be any objection to such a transformation.

Mr. FitzGerald has called attention to a number of things connected with furnaces, and it seems to me the answer to these remarks is that each problem must be carefully studied, and must be considered by itself. Continuous processes should not be generally condemned merely because in some cases intermittent processes are better. It seems to me that each case should be considered by itself on its own merits; to do this is what consulting engineers are for, and if they were employed more frequently as an intermediary between the capitalist, who generally knows nothing about the technical features, and the man who wants to sell him something, it would generally be of great advantage to the capitalist.

JOSEPH W. RICHARDS: I am not an expert on alternating current matters, but I would ask the question whether the straightening out of the distortion of the wave in using large currents is not greatly due to the volatilization of silicon, silica or lime, thus changing the character of the arc.

C. A. HANSEN: Dr. Richards calls attention to the long arcs such as are in the Stassano furnace. These long arcs are due to the ionizing action of the basic slag carried in the furnace. If he will try an acid slag in the same furnace, he will not find the same condition of long arcs at low voltage.

Last fall Dr. Richards spoke of the long arcs in the zinc furnace of the Weeks type. It so happens that in the Weeks furnace, when the furnace was working normally and full of zinc vapor, 200 volts barely sufficed to keep an arc ½ inch long. Zinc vapor is an extremely poor conductor at atmospheric pressure.

It is therefore true that the nature of the furnace atmosphere has all to do with the nature of the arc. Slag may, however, act as a catalyzer or ionizing agent upon the gas in the furnace without in itself taking part in the conduction of current. This is merely the old case of the hot lime cathode rectifier.

A lecture delivered by invitation at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914, President E. F. Roeber in the Chair.

ELECTROLYTIC FLAMES.

By Wilder D. Bancroft and Harry B. Weiser.

If a sodium salt is introduced into the flame of a Bunsen burner, the flame becomes colored yellow. Since this result is obtained with almost any sodium salt, it seems at first as though the yellow flame were characteristic of the presence of sodium in any form. This is not true, however. The introduction of hydrochloric acid into the yellow flame cuts lown the intensity very much. With sodium chloride in a hydrogen-chlorine flame, it is possible occasionally to obtain a flame which does not show the characteristic sodium lines, even though the temperature of the flame is considerably higher than that of some non-luminous gas flames which do show sodium lines. The reaction with sodium salts is so sensitive that it is not a satisfactory one to study. We get the same general results in a simpler form with the copper salts. If an aqueous solution of copper chloride is sprayed into the flame of a Bunsen burner, the flame is colored green; but if a solution of cupric chloride in aqueous hydrochloric acid is used the flame is blue with a reddish tip. The usual explanation is to say that the green flame is due to copper and the blue flame to cupric chloride.

While this is a plausible hypothesis, there ought to be some independent confirmation of the presence of metallic copper in the green flame and of the absence of metallic copper in the blue flame. It has turned out to be unexpectedly easy to furnish this proof. There is no theoretical reason why copper should not be present in the green flame. All exothermal compounds become less stable with rising temperature and at some temperature the copper salts must break down into copper and chlorine, oxygen, or something, depending on the salt taken. The only question is whether this dissociation is perceptible at the temperature of the Bunsen flame. We can test this by introducing into the colored

flame a porcelain tube through which cold water is running. In this way the dissociation products will be cooled so rapidly that there will be relatively little recombination. From the green flame a copper mirror is obtained and from the blue flame a precipitate of copper salt. It may be urged that the metallic copper is due to reduction by the hot flame gases; but this is not so, because the deposit is obtained best from the hottest portion of the flame, which is not a reducing flame. By using a Smithells separator, it is possible to arrange things so that the copper salt never comes in contact with the reducing portion of the flame at all.

This arrangement of a chilled tube held in the flame is merely a special form of Deville's hot-cold tube. By means of it we have obtained mirrors of zinc, cadmium, tin, lead, bismuth, antimony, arsenic and silver. We do not get mirrors of metallic molybdenum and tungsten when the corresponding oxides are held in a flame of a Bunsen burner. According to the theory this shows that the temperature of this flame is not high enough to cause sufficient dissociation. Consequently we tried the oxy-hydrogen flame and succeeded in getting satisfactory mirrors of tungsten and molybdenum in this way. Another interesting thing is that sulphur dioxide dissociates in the hydrogen-air flame so that we can obtain a precipitate of sulphur. If sulphur dioxide is led into a Bunsen flame one can also precipitate sulphur; but the experiment is not a satisfactory one because the sulphur comes down black owing to the presence of carbonaceous matter.

Sodium and potassium salts introduce a special difficulty. It was hardly to be expected that we should get mirrors of metallic sodium and potassium. We have some evidence, however, that the metals are actually precipitated. The sodium chloride, precipitated from the hottest flames, is distinctly alkaline. At first sight it would seem as though this were due to hydrolysis in the heated gases. Caustic soda is more volatile however than sodium chloride and consequently should be found in larger amounts in the outermost portions of the flame. This is not the case, since the sodium chloride from the outside of the flame is neutral. The greatest alkalinity is obtained under the conditions where we should expect to have the largest amount of free metal. While

this is not absolutely conclusive as to the presence of free sodium metal in the flame, it is so exactly in line with what has been proved for the other metals that further experiments seemed unprofitable.

Having proved that we have metallic copper in some flames, we necessarily conclude that a continuous series of dissociations and recombinations is taking place and we ask ourselves what effect these reactions may have upon the light emitted by the flame. We know that certain reactions emit light and that these reactions emit a more intense light when speeded up.[1] A good experiment to illustrate this is the oxidation by hydrogen peroxide of phosphorus dissolved in glacial acetic acid. Vigorous stirring increases the brilliancy considerably. By increasing the reaction velocity it is possible to obtain an emission of light with certain reactions which ordinarily do not give out light. This can be shown by adding concentrated hydrogen peroxide to an alkaline solution of pyrogallol, or formaldehyde. With dilute hydrogen peroxide there is no emission of light. It is not much of an extrapolation to conclude that probably all reactions give out light if they take place sufficiently rapidly.[2] The problem therefore was to determine what reactions in the copper flame were emitting light and, qualitatively, what light they emitted. Fortunately it was not necessary to develop a new technique. We were quite successful in applying the time-honored method of guessing the reaction and then testing the guess. The following results were obtained for copper salts in the Bunsen flame:

I. Cuprous ion to cuprous salt = red.

II. Copper to cuprous ion = green.

III. Cuprous ion to cupric salt = blue.

The first conclusion is based on the action of cathode rays on cuprous iodide, the third on the combustion of cuprous chloride in chlorine, and the second on the combustion of copper in oxygen. A number of experiments were made on the rapid reduction of cupric and cuprous salts, using sodium and aluminum as reducing agents. No characteristic luminescence could be obtained, presumably because these reverse reactions were not

[1] Trautz: Zeit. Elektrochemie, **10**, 595 (1904); Zeit. phys. Chem., **53**, 108 (1905).
[2] Cf. Bancroft: Jour. Franklin Inst., **175**, 129 (1913).

made to go sufficiently rapidly. However that may be, it is clear that reductions play no important part as regards the light emitted by copper salts in the Bunsen flame. Since we have no adequate data as to the action of cathode rays on cupric salts, we cannot now state what light, if any, is emitted by the change from cupric ion to cupric salt. For the present we cannot differentiate between the change from cuprous ion to cupric ion and the change from cupric ion to cupric salt.

By means of these three conclusions we can account qualitatively for all the phenomena in the copper flames except for the red tip, previously referred to, which is obtained when a solution of cupric chloride in aqueous hydrochloric acid is sprayed into the Bunsen flame. This red or violet portion of the flame is apparently not a true luminescence but is merely the color of cupric chloride vapor. One can get it by itself by heating copper in an electric furnace and then running in chlorine, or by heating anhydrous cupric chloride. This puzzled us for a good while; but I think that we have solved the problem. The reason for the blue flame when hydrochloric acid is present is that the dissociation of the cupric chloride is forced back and that consequently no appreciable amount of free copper is formed. If this view is right, it ought to be possible to get a blue flame with cupric chloride in the absence of hydrochloric acid provided the temperature is kept down. This can easily be done, because the alcohol flame is about on the border line. Cupric chloride in a hot alcohol flame gives a green light; but it gives a blue one in a cooled alcohol flame.

Since the bulk of the light in salt flames is due to chemical reactions and not to temperature radiation, there is a possibility of duplicating the effect if we can cause the reactions to take place sufficiently rapidly at low temperatures; in other words, if we do them electrolytically. Some years ago Schluederberg[3] showed, in the Cornell laboratory, that light was emitted when an alternating current is passed through lead electrodes in sulphuric acid. Later, Wilkinson[4] obtained flashes of light with a number of metals as anodes, using a direct current. Owing to a film formation the light could only be seen for an instant. By

[3] Jour. Phys. Chem., **12**, 623 (1908).
[4] Ibid., **13**, 695 (1909).

pressing a toothbrush against a rotating anode, it is possible to remove the film as it gets too thick and thus to obtain light continuously for an indefinite period, ten minutes for instance. As yet we have not been able to obtain an electrolytic flame with copper which could be shown to a large audience, but we can do this readily with mercury.

When mercurous bromide or mercury is burned in bromine an orange light is emitted. For demonstration purposes it is better to start with mercury because it is more easily handled. When mercurous or mercuric bromide is exposed to the cathode rays a similar orange light is obtained. If one makes mercury anode in a cold, fairly concentrated potassium bromide solution (25 percent for instance) and uses an anode current density of about two amperes per square decimeter, the mercury first becomes coated with a film of bromide and then appears to glow with a brilliant orange light. This will last for at least ten minutes, at the end of which time the film of bromide will have become so thick as to prevent the light being seen. By looking carefully from the side, light can still be seen between the film and the surface of the mercury. The light can be obtained at as low a voltage as three volts but the intensity is then very low. With increasing voltage, which really means increasing current density, the intensity of the light increases, the upper limit coming when visible sparking takes place. The phenomenon is shown very well at a voltage of 24-28 volts. We have used a mercury anode up to eight inches in diameter getting a practically uniform glow over the whole surface. There is no apparent reason why the size of the anode should not be increased indefinitely if one so wishes. Most of our experiments have been made with a mercury anode four inches in diameter. This works well with a current of about 1.5 amperes. Potassium chloride or potassium iodide solution may be substituted for the bromide solution; but our experience is that the bromide solution is rather the most satisfactory.

With the theory in its present form it should be possible to get an orange light when mercury or mercurous bromide is converted into mercuric bromide chemically in aqueous solution; but we have not succeeded in doing this. We have tried bromine

carriers and the action of nascent bromine from hydrobromic or bromic acid without avail. We do not know as yet in what way the theory is to be modified in order to account for this. There is also a difficulty in regard to the electrolytic production of light. The theory does not call for the intervention of a surface film and yet we have no satisfactory case of light being produced electrolytically when no film was produced. This suggested the possibility of sparking or of the silent discharge as the cause of the light. We have coated glass tubes with mercurous and mercuric bromides and have passed the silent discharge through them without duplicating the electrolytic phenomena. Sparking has also not given the desired results. The one hypothesis which we have not tested is that light is emitted when mercury vapor or mercurous bromide vapor reacts with bromine. It may be that there is enough resistance in the film so that either mercury or mercurous bromide is volatilized. In favor of this hypothesis is the fact that it is not easy to get a green flame by burning copper in oxygen owing to the high temperature at which copper volatilizes.

Having obtained a fairly brilliant glow with potassium bromide solution at ordinary temperature, we heated the solution expecting thereby to increase the intensity of the light emitted. Very much to our surprise we found that practically no light was emitted at temperatures above 40°. Conversely, the light becomes more intense for a given current density, the colder the potassium bromide solution is cooled. There are at least two possible explanations for this: one plausible and prosaic; the other improbable but impressive. Since we don't know what part the film plays in the production of the light, we may assume that we get a more suitable film at low temperatures than at higher temperatures, less granular perhaps and more coherent. There is however the alluring possibility that the phenomenon is independent of the properties of the film. In that case the most natural explanation would be to assume that the efficiency of light production increases with falling temperature. In support of this view we have a few facts all of which can be accounted for in other ways.

If iodine vapor is heated to 500° it emits light, undoubtedly

as a result of dissociation and recombination, though this has not been proved conclusively. Above 700° the intensity of the light decreases, though the dissociation is still moderate in amount. Whatever reaction is emitting the light is taking place faster at the higher temperature and the light should therefore be more intense, if there were no decreased efficiency of the conversion of chemical energy into radiant energy. A sufficient hypothetical decrease in the conversion factor would however give us a decrease in the intensity of the light. While we have no proof that this is the true explanation, it is at present the only hypothesis which really attempts to account for the facts.[5] The phenomenon seems to be general, for Stark[6] has shown that the electric discharge through a sufficiently heated gas at low pressure is non-luminous. The same hypothesis of a conversion factor increasing with falling temperature accounts for Dewar's discovery[7] that many substances phosphoresce at —180° which do not do so at ordinary temperatures.

It is hard to tell whether the work of Ramsay and Gray[8] on the liquefied and solidified radiation comes in here or not.

"The liquid emanation is colorless and transparent, like water, when seen by transmitted light; it itself is, however, phosphorescent, and shines with a color varying with the nature of the glass forming the tubes in which it is confined; it might be more correct to say that it causes the glass to phosphoresce. The color varies from blue to lilac; in silica it is blue; in lead-potash glass bluish-green; and in soda-glass, lilac; when compressed strongly in soda-glass, the color reminds one of the cyanogen flame, at once blue and pink. On cooling further, the liquid solidifies, and ceases to transmit light; on warming, it again becomes transparent. This gave a means of determining its melting point, using a pentane thermometer, which registered correctly at the ordinary temperature and at the temperature of a pasty mixture of carbon dioxide and alcohol (—78.3° : Travers, *Experimental Study of Gases*). The actual temperature at which the emanation melts is —71°. On cooling further with alcohol cooled with liquid air, the color of the phosphorescence changes.

[5] Cf. Evans: Astrophys. Jour., **32**, 1 (1910).
[6] Drude's Ann., **1**, 424 (1900).
[7] Dewar: Chem. News, **70**, 252 (1894).
[8] Jour. Chem. Soc., **95**, I, 1079 (1909).

The solid glows with great brilliancy, like a small steel-blue arc light. Further reduction of temperature changes the color and in liquid air it is brilliant orange-red; the color change takes place in inverse order on warming. The red phosphorescence disappears pretty sharply at —118°. All these phenomena were observed with a microscope the objective of which was about one inch focal length."

It is not clear whether the solid emanation emits light or whether it causes the glass to do so. The change in color with changing temperature is more easily understood in case it is the glass which emits the light.

At the other end of the temperature scale, the hypothesis of a lower conversion factor gives a possible explanation of spectroscopic changes which does not necessarily involve dissociation. We quote from Stewart's recent book.[9]

"An examination of nebulæ shows that bodies of this class which are in their earlier stages of existence (those where the gaseous mass has not begun to condense), have a spectrum consisting of three lines, one of which is characteristic of hydrogen, while the other two belong to elements which do not exist on the earth. The older nebulæ, in which the gas has begun to contract into a more compact mass, exhibit the spectrum of helium in addition to that of the other three elements known in the earlier nebulæ. Coming now to the stars, we find that they may be grouped into five main divisions. First come what are termed the helium stars, intensely luminous, and containing hydrogen, helium, oxygen, nitrogen, and magnesium, along with traces of other elements. The next series, the Sirian stars, shine with a brilliant white light, and their spectra show the presence of iron. The sun is the prototype of the third class; it contains a very large number of metallic elements. The fourth type of star is termed the Antarian, and in it the elements present in the sun are also found, but titanium appears to exist in the Antarian star to a much larger extent than in the sun. Finally, we come to the carbon stars, which are red, and rather faint in their appearance. In this series carbon makes its appearance accompanied by calcium and other metals.

[9] Stewart: Chemistry and its Borderland, 200 (1914).

"Now, if we take these data at their face value, it would appear as if there was no relationship between the composition of the nebulæ and the composition of the stars; for the nebulæ do not contain many elements which are present in the stars. On the other hand, if we follow the nebular hypothesis, we are driven to conclude that the materials of the nebulæ are the same as the materials of the stars, with this difference, that the temperatures in some of the nebulæ are probably much higher than in the more solid star masses.

"Instances are actually known, and have been studied spectroscopically within recent years, in which two invisible dark stars have collided and flashed into vapor on their impact. Such phenomena put our first assumption out of court; we cannot assume that there is a difference in composition between stars and the nebulæ arising from them. What, then, can account for the difference in composition of the stars and the nebulæ? Clearly we must conclude that when the elements of the colder stars are raised to the extremes of temperature which exists in the nebulæ, the complex elements, such as iron and carbon, disappear as such, and become disintegrated into the simpler substances—helium, hydrogen, and other light elements.

"Taking this as a working hypothesis, we shall find that there is a steady increase in the complexity of stellar composition as the stars cool down. Beginning with the early nebulæ, we find present only hydrogen and an unknown gas; with the cooling of the nebular mass, as condensation of the gas takes place, helium is formed from the simpler elements; by the time the gaseous material has become consolidated into the form of a hot star, oxygen and nitrogen have come into existence in large quantities; and we can trace the further progress of this synthesis of the elements until at the cooler end of the scale we come to the production of large quantities of carbon in the oldest stars. This hypothesis of stellar evolution is largely due to Sir Norman Lockyer, and it will be seen that it pictures the chemical atoms growing during the cooling of the primal ultra-atomic vapors, just as a visible drop of rain grows by the condensation of invisible particles of water vapor."

It is possible to account for the disappearance of lines at very high temperatures either by assuming, as Lockyer does, that the

elements, which normally produce those lines, do not exist at the high temperatures or by assuming that these elements do not emit light at these temperatures. This illustration shows how important it is to find out the real reason why the mercury anode does not emit light when the temperature of the solution rises. If the phenomenon is due to a change in the conversion factor of chemical energy, we can also account for a number of apparently unrelated phenomena without making any further assumptions. If the difference is due solely to a change in the physical structure of the film over the surface of the mercury, no striking conclusions can be drawn at present.

Cornell University.

DISCUSSION.

CARL HAMBUECHEN: The work of Dr. Bancroft calls to my mind a number of experiments I performed a number of years ago in connection with an aluminium rectifier. When you place two aluminium wires comprising the two electrodes in a sodium phosphate solution and apply a pressure of 50 to 100 volts across the two electrodes, practically the same kind of a light will be emitted. It is similar to the light emitted from phosphorus, and it may be interesting to have Dr. Bancroft explain why this phenomenon occurs with aluminium electrodes.

W. D. BANCROFT: The two cases, I think, are quite dissimilar, because in the case of the aluminium rectifier you have a very large potential drop right at the electrode, and you unquestionably get sparking; if you examine the electrode carefully you can see the sparks. I have not examined the mercury electrode under the microscope, but we are doing the experiment on a four-inch circle, and to the eye the light looks uniform, the limit of intensity being at the point where you can see sparks.

I am not prepared to say that there is not a sparking here, because I do not know how to test it.

Dr. Whitney told me the other day that he had seen the aluminium rectifier working at low current and apparently producing a uniform glow; but sparks were seen under the micro-

scope. It is possible that under the microscope sparks could be seen here. I have not tried that.

CARL HAMBUECHEN: The light from an aluminium rectifier is a phosphorescent light and does not consist of sparks; you can get substantially the same results from lead electrodes in sodium bichromate solution.

W. D. BANCROFT: We have obtained light with an alternating current in sulphuric acid between lead electrodes. If you use alternating current the lead sulphate is detached and the solution is filled up with lead sulphate, and you not only get light from lead electrodes, but reflected from the lead sulphate.

SAMUEL A. TUCKER: What effect has the current density on the light intensity in this experiment?

W. D. BANCROFT: The light increases with the current density. With a low current density the light is very faint. If you increase the current density you get increasing brilliancy with, qualitatively, the same kind of light; the limit of intensity is the point where you begin to get sparking from the mercury in the film.

SAMUEL A. TUCKER: At about what current density are you operating now?

W. D. BANCROFT: We were running at about 2 amperes per square decimeter, that is, a 4-inch circle, and a current about one and one-half amperes.

EDWIN F. NORTHRUP: It has been reported in Metallurgical and Chemical Engineering that a party in England has very much increased the chemical activity of batteries by superimposing on the direct current a rapid alternating current. It occurs to me to ask Dr. Bancroft, if he were to superimpose a high frequency alternating current on the direct current, might not the chemical activity be increased, resulting in the production of more light? Have you made the experiment?

W. D. BANCROFT: Would it not be better to confirm the experiments you quoted first?

EDWIN F. NORTHRUP: My impression has been that this report is correct, since it appeared in a technical journal, and not in a newspaper. (Laughter.)

E. F. ROEBER: I do not know to what particular report Dr. Northrup refers, but I know that the superposition of an alternating current on a direct current is in successful use in connection with the Wohlwill process in gold refining in Germany, and has considerably extended the range of alloys which can be treated by this process.

W. R. WHITNEY: I would ask Prof. Bancroft whether the iodine shows any phosphorescence at all?

W. D. BANCROFT: Wood has done a lot of work on fluorescence of iodine vapor. Whether it actually shows phosphorescence, I do not know; in fact, it seems to me to be distinctly difficult to tell about that, because if you heat the iodine to 700°, turn off the current, and let it cool down to 500°, it will continue to glow. I do not know whether you would call that phosphorescence or not.

W. R. WHITNEY: If it persisted after the wire cooled, I would call it phosphorescence. I think possibly the explanation of the experiment as shown may be that you get a reflection from the particles of condensed iodine near the platinum wire.

W. D. BANCROFT: In this particular form that might happen, but in the form as originated by Evershed and also Konen, they took all those things into account. I think there is no question about the fact that at the higher temperature the iodine emits less light, because there has been a pretty careful quantitative spectrum study of the thing.

As I said, I do not see how one could classify it as phosphorescence, as long as you keep the temperature above the glow point, because you have this chemical reaction. It is possible that you might heat iodine to 400°, and that when exposed to a bright light it might emit light. Then you get back to Wood's experiments on the fluorescence. I think it is all a matter of definition.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

ELECTRIC STEEL CASTINGS.

By C. A. Hansen.[1]

During the summer of 1911 a 3-phase arc furnace, having a nominal capacity of two tons per charge, was installed in a new and modern foundry of the Treadwell Engineering Company at Easton, Pa.

The current supplied at 2200 volts, 60 cycles, was stepped down to furnace voltage (85) by means of two 200 K-V.A. transformers connected in open delta. For the sake of greater flexibility than is ordinarily offered by alternating current motors, a small 5 Kw. motor generator was installed, and direct current motors were used for regulation of the electrodes. Transformers, switchboards and furnace, together with a pair of bottom-pour ladles and suitable heating rig for them, constitute the entire melting and pouring equipment.

The whole occupies a floor area not exceeding 300 square feet, inclusive of working space.

No source of molten steel has been provided for the foundry other than the 2-ton electric furnace, nor has a spare furnace been found at all necessary to guard against failure of metal supply due to irregularities of operation or maintenance of the one-unit melting equipment.

The Treadwell Engineering Company management had previously operated a crucible steel castings foundry (Lebanon Steel Castings Co.), and took over the work of the old crucible plant, mainly light section castings.

The cost of melted metal from the electric furnace was found to be somewhat less than one-half that of the old crucible furnace plant when the latter was using oil at 2½ cents per gallon. Since the advance in the price of oil has added $6.00 to $7.00

[1] Published with the permission of Mr. M. H. Treadwell, President of the Treadwell Engineering Company.

more to the cost per ton of molten crucible steel, the possibilities of saving in costs is readily apparent.

So far as the product is concerned, the most striking differences are not found in comparing electric and crucible steels of similar composition. If any differences exist between such steels, they are negligible in importance, as repeated tests have shown.

Electric steel castings are usually made in lower carbons than it is possible to make from even clay-lined crucibles. In the latter it is perfectly possible to melt 0.20 carbon steel, but it is not possible to run the 0.20 carbon product regularly into light-section castings. As a result, 0.30 to 0.40 carbon castings are the usual output of the crucible steel foundry, and all castings which require machining must be annealed.

With the electric furnace, furnace maintenance costs increase rapidly as the carbon content of the product is brought down, and, quite contrary to current opinion, it is not economical to turn out 0.10 carbon steel castings, although it is perfectly possible to do so.

It is, however, economically practicable to turn out 0.20 carbon castings, and such castings can be machined easily without annealing. There is little question that all castings, whether 0.20 carbon or 0.30 carbon, can be improved by annealing, but the American attitude seems to be against the expense of annealing where annealing can be avoided.

Current opinion also has it that the advantages of the electric furnace follow largely from the fact that such a furnace can work up any sort of a charge. While this may often be true, it is not well to base estimates of the cost of molten electric furnace steel upon the usual published furnacing costs and upon the local prices of stove-scrap and similar materials.

Probably every operator of an electric steel furnace has at one time or another run off heats from charges composed of stove-scrap or its equivalent, and little need be said of the reasons for or against such a procedure.

Many have suggested charging molten cupola metal directly into the electric furnace for refining. In several such cases of which I know, the power consumption per ton of output was greater for the cupola metal charge than for the cold scrap charge; the original cost of the cupola metal was in the neigh-

FIG. 1.

UNIVERSITY OF

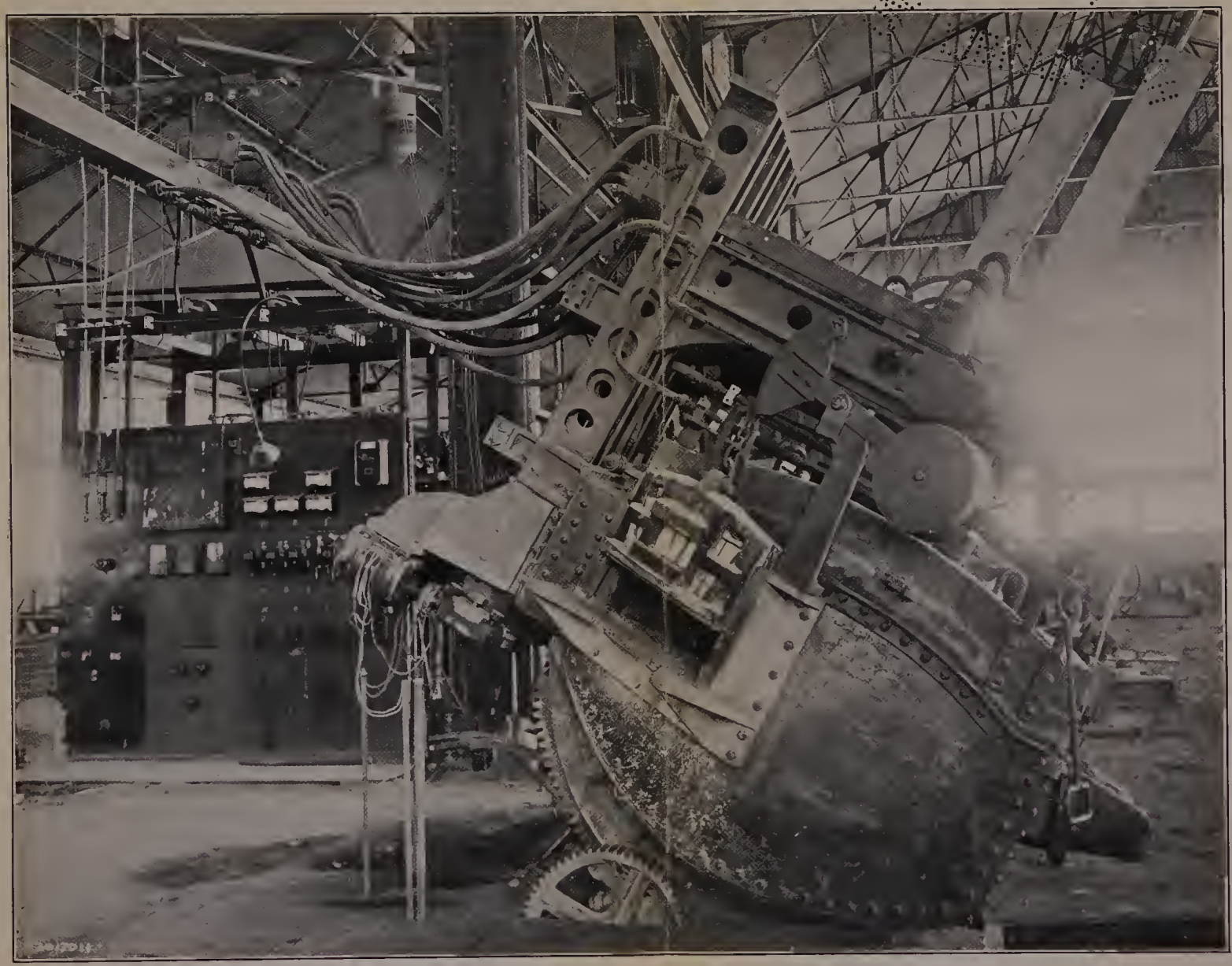


Fig. 2.

borhood of $18.00 per ton, as compared with $12.00 per ton for the regular cold charge, and the cost of furnacing was likewise higher for the cupola metal charge. The economy incident to heating the furnace with auxiliary fuel-burning apparatus may interest those who charge molten metal into electric furnaces, but the interest attaches rather to the prevention of skulled furnace bottoms than to a direct saving in electric energy. Heating the furnace and charge to a good red heat by means of oil burners (with oil at 2½ cents per gallon) increased the cost $1.00 per ton over the regular practice of all-electric heating. Keeping the furnace hot over night by means of either oil or electric energy was found not to materially decrease maintenance costs, and it did increase the cost of production. These items above refer to power supply at approximately one cent per kw. hour.

Much stress has been laid on the economy attaching to continuous operation of the electric furnace as compared with mere day-shift operation. So far as costs go for the molten steel, it is true that continuous operation means 10–15 percent saving over intermittent operation. Very little has, however, been said regarding the relative efficiencies of day and night work in the other departments of the foundry, nor has it been well impressed upon the mind of the average investigator of electric steel problems that one can easily lose many times the 10–15 percent saving in molten metal costs in the decreased efficiency of the night shifts on the moulding floor, cleaning room, etc.

Claims are being made that 10 to 12 heats from cold scrap can be taken from one electric furnace in 24 hours. Possibly they can, but the furnace will have to be rebuilt at least three times each week.

These and other considerations have led to the practice, now established at Easton, of operating the foundry on day shift only, charging a good quality of steel scrap, enough pig and ore being added to keep the charge off the furnace bottom, and casting steel of around 0.20 carbon, unless otherwise specified.

The furnace plant has been operated on a one-heat-per-day basis, requiring 7 to 7½ hours to turn out its charge from the cold furnace. Power consumption at furnace transformer primary terminals has, in that case, averaged 1050 kw. hours per 2000 lb. (909 kg.) steel in the ladle.

The furnace has been operated also on a two-heat-per-day and three-heat-per-day basis, when business conditions warranted. The second and third heats, having the advantage of being started off in a hot furnace, are finished in 4½ hours, at a current consumption of 630 to 640 kw. hours per ton. Even with the three heats per day, no steel is poured outside of the regular day shift. Two men start the furnace shortly after midnight, and steel is poured at 7.15 A. M., 11.45 A. M. and at 4.30 P. M. The uncertainties attaching to pouring on schedule time are not as great as they are with either open-hearth or crucible furnaces.

Much has been written, especially by electrochemists familiar with direct-current electrolytic apparatus, regarding the undesirable character of the loads taken by arc furnaces. It may therefore be well to state that the load curve for the furnace here considered is smoother and of higher power-factor than the load of similar magnitude used in the shops of the Treadwell company where the products of the steel and iron foundries are machined.

It seems a pity that the electric steel furnace was not developed by people familiar with the load characteristics of modern machine tools, rolling mills, street railways, etc., etc. Central stations are quite familiar with these loads, but they are not familiar with the arc furnace, so when we dwell upon the bad features of the arc-furnace load we can scarcely blame the central station for supposing the load-curve of the latter to be a really bad one.

ADDENDUM.

Since the above was written, Mr. Treadwell has sent the following additional data concerning his furnace:

Average number of heats per week	15	
" weight per heat	4,600	lb.
" power consumption per 2,000 lb	900	Kw. Hr.
" repair costs per 2,000 lb	$2.50	
" electrode costs per 2,000 lb	$2.50	
" weight castings made	9	lb.
Ratio of cleaned castings, risers, etc., to charged weight	92-95%	
" finished castings to charged weight	approx. 60%	

The furnace lining is repaired after 35 heats.

Mr. Treadwell is a firm believer in pouring extremely hot steels, and this fact is reflected in the high maintenance costs and in a rather high power-consumption.

A similar furnace, of which I have accurate records, shows costs as follows:

Power consumption per 2,000 lb	725 Kw. Hr.
Repair costs per 2,000 lb	$1.30
Electrode costs per 2,000 lb	$2.15

The latter furnace is pouring somewhat colder metal into castings of 15 lb. average weight, and repairs to the furnace lining are made after 8 to 10 weeks' operation on the same basis of 15 heats per week. In the latter case the repair charges include upkeep of the bottom-pour ladles used, and I believe this is also the case with Mr. Treadwell's figure.

Research Laboratory,
General Electric Co.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

ELECTRIC FURNACES FOR STEEL MAKING

By E. B. Clarke.[1]

The intending user of an electric furnace wishes dependable answers to two questions:

First. How will an electric furnace compare with some other apparatus for producing or refining steel as to quality of output and cost of operation?

Second. Assuming the wisdom of an electric furnace installation, what is the best type of furnace, and what size of unit is proper?

Most of the available literature upon these subjects is of a theoretical nature. Information from a practical standpoint will generally be acceptable, but when one is actually a user of electric furnaces in the commercial production of steel he does not find a great deal to say. After all, this is not a surprising fact, for the electric furnace does not offer anything radically new in the production or refining of steel. Its use is generally contemplated for a purpose where steel may be made or refined either in an electric furnace, a crucible furnace, a Bessemer converter, or an open-hearth furnace.

The crucible furnace enables one to make accurate alloy mixtures of high quality without contamination from gases or furnace linings. Practically no refining can be done and therefore high grade materials must be used for the mixture. By the law of supply and demand, the price of pure materials for use in crucible furnaces will be higher where the crucible process is employed to a considerable extent. The electric furnace will produce steel of the same degree of purity as a crucible furnace, and the possibility of refining in an electric furnace makes possible the use of less pure materials. This is an advantage for the

[1] President, Buchanan Electric Steel Co., Buchanan, Mich.

electric furnace and, at the same time, helps the crucible furnace, because the demand for the high grade materials necessary in the crucible process is reduced by each additional electric furnace installation and therefore the price of the charge for the crucible furnace is reduced. This is especially true as applied to the small crucible furnaces used in foundry practice, which require low-phosphorus steel punchings for their successful operation.

The side-blow Bessemer converter is capable of producing hot steel in small units quickly. It does not permit of refining, however, and therefore necessitates the use of low phosphorus and low sulphur pig iron which must be pre-melted in a cupola, using high grade coke. The losses are severe and the steel is not free from oxides and occluded gases. The electric furnace will produce steel just as hot as the small Bessemer vessel, but free from oxides and occluded gases. However, the electric furnace requires scrap for charging rather than pig iron, so if only pig iron is available at commercially desirable figures, the pig must be converted into steel before charging into the electric furnace.

The open-hearth furnace will produce from pig and scrap, steel of a fairly high degree of purity and of fairly high temperature. The electric furnace will do the same thing (except that the use of a large percentage of pig is not desirable) and is capable of producing purer and hotter steel than is the open-hearth under usual operating conditions.

Summarizing these general observations, it may be said that, although the electric furnace really offers nothing that the crucible furnace does not as regards the alloying of steels, although the electric furnace cannot produce hotter steel than does the Bessemer converter, and although the electric furnace really offers nothing that the open-hearth does not as regards the refinement of steel, still it is true that the electric furnace combines in itself the advantages of all three of the other processes mentioned. This is the important advantage of the electric furnace.

Of course, it is seldom that one wishes to secure the advantages of *all* these other three processes combined in one. Generally, a certain object is in view by the intending user of an electric furnace or some other form of apparatus for producing steel. Of course, broad generalities will not solve this problem. The cost of production is the final answer from a com-

mercial standpoint, and this depends not only upon the market for the intended output, but upon the available supply of steel making materials, and upon the availability of a satisfactory and sufficiently cheap source of electric power. In passing it might be observed that this question of electric power supply is generally not so serious as might at first appear. In the first place, there are many locations where a sufficient amount of fairly cheap electric power may be purchased; and in the second place, the item of power is not often of supreme importance.

There are other elements entering into the production of electrically refined steel which have a far greater influence on the cost of production than is generally credited. The most important of these is experience. It should be understood clearly that the electric furnace is a more delicate apparatus than any of the other three furnaces mentioned. It is more difficult to handle and its operation offers more likelihood of mishaps. Electric furnace operation has not yet been reduced to standard practice. Melters familiar with its operation are scarce and difficult to find.

To attempt an answer as to what type of furnace is best is as unsatisfactory as to make general comparisons between electric furnaces and other furnaces. If we could accept at face value the statements of a number of men interested in the development of certain electric furnaces, we could easily believe that as soon as a foundryman had installed an electric furnace (provided he installed the right one) his troubles would be at an end. As a matter of fact, he is apt to find that they are just beginning. In the first place, unless the design of the furnace has been thoroughly tried out in practice, it will certainly have to be modified considerably from the designer's ideas. In the second place, the user will certainly find the furnace to be a more delicate piece of apparatus than he had anticipated. He will find that while he can make steel of a very high quality, he can also make, without difficulty, much steel of a very low quality. If there are in the Society some men who have been using electric furnaces for the production of castings or special steels, they will have no difficulty in recognizing these remarks as coming from one who has also had such experience. It so happens that the speaker's experience has embraced not only a study in this country and Europe of the design and operation of a number of different types

of furnaces, but has embraced the actual operation of two typical types of furnaces for the production of steel castings. The investigation as to which general type of furnace is best led in my case, as in that of most others, to much confusion of ideas. It is so evident that each type has certain advantages and disadvantages, and so impossible accurately to gauge the proper importance of the various advantages and disadvantages, that one cannot reach a conclusion as to which type of furnace is best, with confidence in his conclusion. Perhaps the only way to learn is to try them all. As a matter of fact, the speaker has already tried two, and may not yet have learned all he can.

We have operated two furnaces of one to one and a half tons capacity each, of the surface-arc type. This general type is best exemplified by the Stassano furnace, the general construction of which is well known. Our furnaces use three-phase power and the arcs are maintained above the surface of the bath. They are lined with magnesite brick, which, of course, while a high refractory, is quite susceptible to damage by sudden heat changes. Very hot and very good steel has been produced in these furnaces. The cost of repairs has been rather high, due to necessity for relining rather frequently. We have found that linings last, under proper treatment, about forty to fifty heats, though we feel that some changes in methods of construction would increase the number of heats per lining and, therefore, decrease this item of cost very considerably. The labor cost on these furnaces has been found to be rather high, but this is partly due to the small capacity of the furnace. The power costs have not been high when the furnace has been operated continuously, even despite the small capacity of the furnace. Where commercial conditions have made it necessary to permit considerable time to intervene between heats, the power consumption has been increased, due to the necessity of keeping the furnace fairly hot between heats. Experience in operation, however, has made it possible to reduce this item of expense far below what was originally believed possible. Even where the furnace is operated on day turn only and kept hot over night with current, the power consumption was surprisingly low for so small a furnace. Electrode costs have been quite reasonable.

Summing up, it may be stated that the operation of these

furnaces has been quite satisfactory, as regards quality of output, reliability of operation and cost of production, when the size of the furnace is taken into consideration. Two furnaces should be used alternately, so that ample time can be allowed for relining, without interfering with the continuous supply of hot metal.

The increasing demand for hot metal for foundry purposes led us to consider the installation of additional metal-producing capacity. We consider that the type of furnace which has just been described is not suitable for units above from two to two and a half tons capacity, because of the increasing difficulty which probably would be experienced with linings in the larger sizes. As a furnace of approximately five tons capacity was necessary, we decided to install one of the submerged-arc type, represented by such furnaces as the Heroult and Girod. A Heroult furnace was put in and has been operated very satisfactorily. Power consumption has been less than in the smaller furnaces, but only by an amount which would be expected for the difference in size of the furnaces. As a matter of fact, claims for low power consumption by any furnace should be received skeptically. It is a fact that the power consumption of any electric furnace depends somewhat upon the efficiency of the furnace, but it also depends to a far greater extent upon the method of operating the furnace. The furnace efficiency depends upon the thoroughness of the heat insulation, for after all, the only heat which is lost is that which escapes by radiation or conduction. That which goes out in the slag, or in the steel, depends not upon the efficiency of the furnace, but upon its mode of operation. Where a high degree of refining is necessary, slags must be taken off, at the cost of power consumption. Where the furnace must be operated with considerable time between heats, heat is escaping rapidly during that idle time. Where heats must be held in the furnace, or melted slowly, to meet a definite schedule, a high power consumption must be expected. For these reasons it appears that the claims for low power consumption of certain furnaces are practically valueless from an operating standpoint. The conditions of operation, rather than the type of furnace, are what control the power consumption, though, of course, the construction of the furnace, as regards heat insulation, does have some influence.

In our five-ton Heroult furnace, we have found the cost of

repairs to be lower than in the smaller furnaces. This is due largely to the type of furnace, but our experience in the operation of electric furnaces has also helped in this respect. Furthermore, we expect to do still better as to repairs. The labor costs are less on the larger furnace, as might be expected, partly because it is automatically controlled, and largely because of its increased output. To summarize our views upon the relative merits of the two types of furnaces, as based upon our own experience, I would say that we have found the surface-arc type to be a much better furnace than its critics would have one believe. On the other hand, we have found the submerged-arc type better for our purposes because of its larger capacity and lower cost of operation.

No attempt has been made here to give actual figures of operation. This is not due entirely to reluctance to publish our costs of production. As a matter of fact, the costs of production are so much dependent upon local conditions, such as quality of scrap available, continuity of operation and price of electric power, that results obtained in one installation, if used as a basis for other installations, may be most misleading. The predominating influences in this case are the commercial conditions surrounding each separate installation.

In conclusion, I wish to reiterate my statement that an intending user of an electric furnace may expect to learn much more about the furnace by his experience after he gets it than by the statements of someone who wishes to sell him a furnace.

DISCUSSION.

HENRY D. HIBBARD: It would be well if the paper by Mr. Hansen were supplemented by some of the results which show the similarity of electric and crucible steels, particularly those of pulling tests.

The increased cost when oil was used for heating the furnace and charge to redness raises the question as to whether the electric current actually used was paid for, or whether it was paid for by the time it was available whether used or not. It has seemed as if the economical arrangement would be to have two furnaces (or multiples of two), each equipped for oil heating and with one source of electricity. Then the current would be used continuously, that is, for the latter half of each heat, which would greatly diminish current cost. With one furnace and the current used but half the time, the cost of keeping the generator idle but ready to run is a very large part of that when it is actually running.

To judge from the life of their furnaces, electric steel melters have not yet learned the economic limit of furnace temperature which should not be exceeded. An open-hearth melter is constantly held down to the heat that his furnace will stand and which he must not allow to be exceeded. He works within quite a narrow range of temperature from the time his charge is at a melting heat until it is tapped. The fusion temperature of the silica brick of his furnace is about 1700° C., so his hearth temperature, outside of the flame (which is hotter), should be between 1650° and 1675° C. The slag may then be at about 1600° to 1625° C., and the metal from 1550° to 1575° C., which is but a moderate margin above the melting point of the steel to allow it to be cast without undue skull in the ladle.

Electric and crucible steel makers are not confronted by the effects of a too high casting temperature on the steel, the fear of which as well as the safety of the furnace obliges the open-hearth and Bessemer steel maker of non-piping steels to keep his temperatures from mounting too high.

The electrode cost of $2.50 per short ton is amusingly large as

compared with synthetic estimates of cost of electric steel published but a few years ago, in which that item was thirty cents per ton of steel.

The smoothness of the load curve during melting, referred to in the paper, does recall one instance where an electric furnace in this country was served with current from a hydro-electric plant some seventy miles away. The usual charge was molten, but a trial of one heat of cold stock was made. The fluctuations of current were so great while that heat was melting that the whole service of the line was interfered with, other consumers of current complaining that their machines slowed down and then forged ahead in a highly disturbing manner.

ERNEST HUMBERT: Mr. Clarke makes an interesting comparison between the electric furnace and the small converter, the crucible furnace and the open-hearth furnace; but in the first and last paragraphs of his paper he emphasizes an opinion which, it seems to me, he has not made altogether clear.

To quote the concluding paragraph, he says: "I wish to repeat my statement that an intending user of an electric furnace may exepct to learn much more about the furnace by his experience after he gets it than by the statements of someone who wishes to sell him a furnace."

It seems to me that Mr. Clarke should tell the prospective user of an electric furnace wherein the statements of the men exploiting electric furnaces have differed from what he has found in practice.

If these differences apply only to the Stassano furnace, with which Mr. Clarke has had experience, I think we should be told what the points are. If the points of difference apply also to his Héroult furnace, I should be glad to have them explained to me, as I have had considerable acquaintance with this particular furnace, having worked on the Héroult furnace as an associate of Dr. Héroult ever since the year 1900. I have also operated Héroult furnaces in the United States, France, Sweden, England and Canada almost continuously during the last fourteen years. The performances of some sixty Héroult furnaces have quite generally borne out the claims made by Dr. Héroult and his associates.

It may be true, as Mr. Clarke says, that the available literature

upon this subject is of a theoretical nature, but the amount of actual data now available upon the performance of the Héroult furnace is very extensive, whether it has been published or not.

One would infer from Mr. Clarke's statement that there was really not much difference between the electric furnace, the crucible furnace, the open-hearth furnace or the Tropenas converter, as regards results.

As far as quality is concerned, it is a generally accepted fact that crucible steel is the standard of the best quality of steel made, but it is well known that the crucible process is not adapted to the making of low carbon steel. It is also quite certain that the cost of crucible steel is far in excess of that of the electric furnace process, and it is now quite generally conceded that electric steel is fully equal in quality to crucible steel.

Mr. Clarke says that, "metallurgically speaking," the electric furnace offers nothing that the open-hearth does not. The electric furnace has one characteristic which, I believe, appeals more strongly to the metallurgist than any characteristic of any other process of making steel. I refer to the fact that in the arc furnace we have a strongly reducing action due to the exclusion from the melting chamber of atmospheric air, and the fact that carbon, which is one of the strongest reducing agents, is used in connection with the slag. This reducing action is so striking that not only is calcium carbide normally present in the slag, but such elements as silicon, manganese, vanadium, tungsten, etc., are readily reduced from their oxides in the slag to the metallic condition in the bath. In the open-hearth furnace the conditions are strongly oxidizing; a flame is continually playing over the bath, and an excess of air is admitted for the complete combustion of the fuel gas used. Open-hearth slags always contain between 10 and 20 percent of iron oxide. Consequently the metal also contains oxides, and it is necessary to use deoxidizers, such as ferro-silicon or aluminum, whereas with the Héroult furnace it is not necessary to add any elements except those which are desired as alloys.

Mr. Clarke says the electric furnace is a more delicate apparatus than any of the other three kinds of apparatus mentioned, and that melters familiar with its operation are scarce and difficult to find. In my connection with the Héroult furnace I have had

occasion to teach a number of men how to operate the electric furnace. These men have not been, as a rule, open-hearth men or crucible men, yet in a comparatively short time, in fact, in about the time it took them to learn how to judge the carbon content by fracture, they were able to run the furnace successfully and make good steel. I think it will be conceded by most of the steel men present that it takes a number of years to train a good open-hearth melter, and that good open-hearth melters are scarce in comparison with the number of open-hearth furnaces in existence. The scarcity of good electric furnace melters is largely due to the fact that there are comparatively few electric furnaces operating, and that the electric furnace is in its infancy as compared with the other furnaces.

As regards the power consumption in the Héroult furnace as compared with that in the Stassano furnace, one would infer that Mr. Clarke attributes whatever difference he has found largely to the difference in the relative sizes of the furnaces. In the Stassano furnace the electrodes are nearly horizontal, and practically as much heat is thrown upward as is thrown downward. This is evident from the fact that it is extremely difficult to maintain a roof on the Stassano furnace, in spite of the fact that it is made of magnesite brick. In the Héroult furnace the electrodes are vertical, and the heat is thrown down into the bath. When these difficulties are considered, it would seem evident that the widely published figures for power consumption, which show a considerable difference in favor of the Héroult furnace, must be at least approximately correct. Mr. Clarke does not give us any figures as to power consumption, but if he does not find a considerable improvement in his Héroult furnace over what he was doing in his Stassano furnaces, I believe that this can be remedied when his operators have acquired the same familiarity with the Héroult furnace that they had previously acquired with the Stassano furnace.

Not knowing the differences in opinion between the seller and the user of electric furnaces which Mr. Clarke has in mind, we are not informed as to what gave rise to Mr. Clarke's opinion regarding these differences, but if this opinion is based upon results as established by his contact with his customers, I can merely say that I know of a number of users of the Héroult

electric furnace who are selling electric steel in various forms and whose customers are apparently entirely satisfied with the product, as evidenced by repeat orders.

As stated above, I think, in order that Mr. Clarke's experience with the electric furnace may be of value to prospective users of such a furnace, he would do all those interested a great favor by pointing out in detail the discrepancies between the statements of "someone who wishes to sell him a furnace" and "the experience which an intending user of an electric furnace" may expect to have.

Considering the very widespread interest now being taken in the electric furnace, such information would not only give the prospective user of an electric furnace what would be of value to him, but would give the man who wishes to sell him an electric furnace an opportunity either to make good on his statements or confess their inaccuracy.

KARL G. FRANK: I want to say that apparently in Germany the experience with electric steel has been more satisfactory than in this country. In the year 1912 about 75,000 tons of electric steel were produced, and in the year 1913, 100,000 tons, a very large percentage of which has been used for electric steel casting, and about 38 to 40 percent of the total, in Austria-Hungary, has been made in induction furnaces. I believe that if the electric steel manufacturers would go into the problem more thoroughly in this country, the results obtained would be more satisfactory.

HENRY HESS: With reference to the remarks of Mr. Humbert that in the Stassano furnace the roof is exceedingly short-lived, I think he is not quite correct. I have had a Stassano furnace in operation for several months, and, while business is so poor that we cannot say we have anything like continuous operation, yet it is a fact that the roof had not shown any sign of distress when it became necessary to reline the hearth and the side walls. It is, therefore, a matter of absolute fact that the horizontal type of arc is not harder on the roof, nor even as hard on the roof, as it is on the rest of the lining.

C. A. HANSEN: Referring to the relative excellence of electric furnace steel and crucible steel, originally, I believe, all

crucible steel was dead-melted, *i. e.*, a certain amount of silicon, sufficient to reduce the metal oxides, was reduced from the crucible, and the metal so siliconized was poured without other additions. Steel so made is comparable with electric steel in that a finished article is delivered by the melting outfit. Now-a-days, however, much crucible steel is killed by additions of ferro-silicon in the crucible or in the larger ladle into which several crucibles have been emptied. The latter method is cheaper in that it reduces both time of melting and crucible cost, but it lays the crucible process open to the same objections that are common to both the open-hearth and converters, in that a half-finished article is delivered by the melting outfit, and that more or less uncertainty attaches to the actual finishing.

My own experience indicates that no especial merit attaches to the fact that a steel is prepared in the electric furnace. Good steels can be made and have been made by all of the above-mentioned processes, and so far as I have been able to judge from comparative tests there is little or no difference between good steels of the same chemical composition prepared by them.

The main advantage in this direction that attaches to the electric furnace is that the composition is under control up to the point of pouring a finished steel, and, with proper management, a better average grade of metal and a more nearly uniform product can be made than with any of the other processes.

Mr. Hibbard referred to certain arc furnaces operating on cold charge that had disturbed the whole service system by reason of load fluctuation. A few weeks ago Mr. Clarke was having that difficulty to contend with. His trouble came from his having operated Stassano furnaces, where he was to a certain extent independent of slag, and his trying to apply the experience gained directly to his newer Héroult furnaces. In the latter case he is not at all independent of slag. He was operating the Héroult furnace with practically no slag; his electrodes were arcing directly to bare metal, and such an arc is notoriously unsteady. His load fluctuated from nothing to 1,000 kw. a dozen times a minute. The addition of a barrel of lime and half barrel of fluorspar in the furnace immediately changed matters so that constant load was obtained.

There is no need of serious power fluctuation for more than

the first 15 minutes of operation in a cold charge, and the troubles will be more in the way of open circuits than in excessive loads.

JOSEPH W. RICHARDS: It was mentioned in the discussion this morning that some electric furnaces are being run with a magnesite roof, not with the silica roof, so that the roofs of all the electric furnaces are not of silica. I saw a Stassano furnace working in Turin with a magnesite roof, and I believe that has overcome the roof troubles. A little further study of the situation may enable us to replace these with a basic roof of more refractory material, such as aluminium nitride, possibly, so as to overcome the difficulties of the silica and its fluxing.

I thoroughly agree with Dr. Frank that European practice in electric furnace work, for some reason difficult to understand, is not reproduced in this country with the same patience and the same mastery of details as is accomplished over there. There is a considerable difference between the perseverance and patience with which the Europeans have solved the difficulties of electric furnace installation and the rather waning enthusiasm which you find here, apparently, amongst our manufacturers; they do not "see the thing through."

With regard to the skill required to run an electric furnace, to which Mr. Humbert alluded, I would call attention to the fact that the furnace at Easton, Pa., which has been running for three or four years, has been for two years in charge of a young man who was a mechanical engineer, who when he came there knew nothing about making steel, and the manager informed me that in the two years since he had charge of the furnace he has not turned out a bad heat of steel. Many of the castings are required to stand U. S. Government specifications. So with the modern electric furnace it is, apparently, not necessary to engage a highly-skilled steel maker to run it.

I would also call attention to the fact that this Easton, Pa., furnace is a good illustration of a furnace used on off-peak power or in the power valleys. They get their power directly from the Easton Power Company, which uses coal and steam engines. The steel works does not use the power between five o'clock in the afternoon and twelve o'clock at night; but the furnace is filled up in the evening, and power is put on at twelve or one o'clock at night; the heat is ready to pour at seven to

nine o'clock in the morning. They get out there one, two or sometimes three heats a day up to about five o'clock in the afternoon. They pay, for the power which they use, one cent per kilowatt hour, and the steel company tells me it is entirely satisfied with the commercial results.

E. L. Crosby: The poor central station seems to have been the all-round goat in this meeting. There has not been a speaker on the floor but has taken his rap at the central station. I do not think, as some of the statements made might imply, that the central station people generally are asleep as to the opportunities in the electro-metallurgical field and the electro-chemical field. The Detroit Edison Company is not. The only real difficulty in the Detroit field is that we cannot find someone who will come and for a specific amount sell a man a furnace.

We have made a rate on electric steel work of approximately three-quarters of a cent or less. We have two or three steel casting people who are interested in the electric furnace, but they find it is difficult to get anyone to come in on a businesslike basis and sell them an electric furnace on the same basis on which they can buy a converter or an open-hearth equipment.

As regards the remarks made this morning, Dr. Hering brought up the question of converters. We would not hesitate to tackle any single-phase furnace there is on the market. We have had some put up to us, and we sort of trembled a bit and thought they were going in. We decided they were not so awful, because almost every central station worries more or less about the power factor on their industrial loads, and many of them care for these demands by synchronous condensers situated at central points.

We would have an excellent opportunity, in the case of a single-phase furnace, going on three-phase power lines, to install a synchronous converter, with over-excited fields, which would not only give us a unity power factor at that particular point, but correct the power factor for that entire territory. We are willing to make that investment ourselves, either in the case of a single-phase furnace, or an induction furnace requiring less than 60-cycle frequency.

I do not think the central station, in so far as I can judge, wants to harrass the prospective electric furnace user with a lot of regulations they must comply with. Our company is willing

to take the burden of furnishing the kind of current the customer wants at a very reasonable price.

F. A. LIDBURY: Someone was asking for information this morning as to the price the central stations were making in the regular all-round load for this sort of off-peak load, and I should be glad if Mr. Crosby would somewhat develop the sample of information he has already given us as to the scale of prices they are talking about.

E. L. CROSBY: The reason I did not get up this morning when that matter was under discussion was that I thought someone might shoot that question at me directly. I have devoted most of my time to just this class of work, and have been traveling around the country trying to find out what are the requirements, and have come to this meeting for the purpose of meeting you gentlemen to determine what the demands for electrochemical and electro-metallurgical service were. We have a rate in Detroit of $51.30 a kilowatt year. That applies all over our territory. In the case of an electrochemical plant being located contiguous to either one of the two generating stations, or in the case of various other things which might enter into the plant operation, that price should be shaded. I am frank to say that at the present time I am awaiting a figure from our management on exclusively valley business. We had not realized the importance of that, because we have not had in Detroit only electrochemical loads, which are usually unity load factor, but there is no question but that a reduction in the rate below that price (I would say, unofficially) of from 15 to 20 percent would be fair for valley business.

C. G. SCHLUEDERBERG: A further word about the furnace at Latrobe: I am not personally interested in it in any way, but simply state what we saw there. As regards power factor, I was very much surprised to see that the power factor was almost unity, and I understand that this has been partially accomplished by properly interlacing the leads going from the transformers to the furnace. I think that information will be of interest in line with the discussion we had this morning on the power factor.

E. L. CROSBY: Mr. Hansen spoke of the fluctuation in current not being any greater at the General Electric plant with the

furnace load than with the industrial power load. One reason we are not frightened about the power factor is that any of the furnace companies guarantee that they can get an 80 percent power factor, which is better than we have attained on most industrial loads.

EDWIN F. CONE: The Society is discussing the subject of steel castings and the electric furnace in reference thereto, and I want to call attention to one or two points which have possibly been overlooked. If you are going to compare the electric furnace for steel castings with any other method of making steel castings, consideration should be given to the refining power of the electric furnace as compared with any other furnace for making steel castings, whether open-hearth or the crucible or the converter. It reduces the sulphur, and also makes a quality of metal which, so far as composition is concerned, is away ahead of anything you can get by any other process, the crucible included, and much ahead of the ordinary crucible steel castings of today, which many of us know are not always what they ought to be.

Another point in regard to the physical properties of steel made in electric furnaces as incorporated in steel castings. In comparative tests of electric furnace steel with those made by any other process, other conditions being equal, as to heat treatment, simple annealing, or some other heat treatment, like quenching, etc., the physical properties are superior. For a given composition the tensile strength is not only higher, but the elastic ratio is much higher. In some electric steel I know of and tested myself, the elastic ratio is even as high as the ordinary acid open-hearth steel with vanadium in it, which is quite striking, I think. In addition to that, the dynamic qualities of electric steel excel those of steel by all other processes.

HENRY HESS: We make electric steel castings, and we also make crucible steel castings. We would be pleased if we could convince our customers that the electric steel casting is better of fundamental necessity. The advantage which the electric furnace has—and it is an undoubted advantage—is that we know very much better what we are going to get out of it than we do with the crucible. From our crucibles we absorb an indefi-

nite percentage of carbon. When we turn the material out with the electric steel furnace we do know what we are going to get, within small variations. Owing to the fact that we control our heat better, we can kill the metal a little better than in the crucible. Anyone who makes the statement that you can get a higher elastic limit or higher tensile strength or better physical quality in the ingot in the end, just because you have electrical heat for melting the steel, is mistaken. The steel does not care by what agency you heat; it cares only for the heat. If you give it the proper amount of heat, at the proper time, you get the proper result.

WILLIAM D. MAINWARING: It does not make any difference whether you make the steel in the electric furnace or in the open-hearth furnace, you have to mix the steel properly and take into consideration the time factor, which is a great factor indeed. I have had fifteen years' experience in steel making, which included about every type of steel that is made, and I have seen some of the poorest steel made in the electric furnace, and seen some of the best. You have to work the steel right, whether you make it in the electric furnace or in the open-hearth furnace.

K. G. FRANK: If one who has listened to this discussion should undertake to draw conclusions from it, I think he would be somewhat at a loss, and that is, in my opinion, mostly due to the fact that too many general statements have been made. If the gentlemen who have discussed the question had defined just a little more exactly what kind of steel they referred to, and under what circumstances the steel is made, under what conditions the cost has been computed, then I think we would have a much clearer picture of what has been done, and the experience obtained, than we have at the present time. Mr. Carnegie, who knew "a little" about steel making, said there are just as many ways of computing the cost of making a ton of steel as there are methods of killing a cat.

JOSEPH W. RICHARDS: Mr. Hess' statement that all the steel needs is heat, and it does not matter which way it is melted, either in the crucible or in the electric furnace, should not go without some qualification, because the electric furnace has

conditions which cannot be duplicated in the crucible melting. There are conditions of higher temperature, greater reducing action and particularly of greater chemical reducing action.

I think a study of the recent literature published, particularly in Europe, will show that the statements which were made by Mr. Cone are true in the main, that under the same conditions steel of the same composition made in an electric furnace has some slightly superior qualities to the crucible and open-hearth steel of the same composition. I think that is a fact shown by the literature.

HENRY HESS: I did make the statement that the advantage of the electric furnace *versus* the crucible lay in the control of the composition of the steel; also that steels of the same chemical composition, whether produced in the electric furnace or produced in the crucible, would have no essential physical differences.

EDWIN F. CONE: It is an established fact that the purer the material, the better its physical qualities. It can be proved, and has been proved, that the electric furnace purifies, whereas the crucible does not, and, relatively, you get what you put into the crucible, and you get better than you put into the electric furnace. It is simply a matter of taking the two and comparing them. The Treadwell furnace at Easton, Pa., has been spoken of, and is the subject of Mr. Hansen's paper. There have been tests made on steel from that furnace published in *The Iron Age*, May 29, 1913, and these tests generally show physical qualities far superior to the crucible, and even superior to the acid open-hearth, the basic open-hearth or converter.

HENRY HESS: I ask whether two steels, one produced in the crucible furnace and the other produced in the electric furnace, which show the same analyses, have not the same physical qualities? The electric furnace gives you more definite control of the final analysis than the crucible. The crucible gives practically no control, but it is a question of what you have in your steel finally that governs its quality, not by what heat agencies it has been melted.

The statement has been made on the floor today, and is also more or less generally made, that electrically melted steel is superior; these statements are very interesting, but would be

more so if justified by reasons. Personally, I feel convinced of the fact. Also, I know that you usually bring out the other man's views and reasons by disagreeing with him, so I did that flatly. However, electrochemists seem to have a different psychology, since the two assertors of the superior physical quality of electrically melted steel merely met the doubt with a repetition of the original statement. As they agree with my own opinion that electric steel is better, I hope they agree also with my reasons, or, failing in that, that they will provide us with better reasons. The ability to control the heat, both as to amount and duration, which ability is inherent in the electric control, carries with it the definite ability to control the chemical makeup of the bath. This definite heat control also makes it possible to hold the bath at a definite temperature for any length of time, and so supplies the ideal conditions for freeing the bath from gases to a far greater extent than is otherwise possible.

HENRY D. HIBBARD: In continuation of what Prof. Richards said, and the question that has been raised about the three processes, the open-hearth, the crucible and the electric, something should be said about the method by which these three processes are carried on. In this country the crucible process is carried on almost exclusively in graphite crucibles. The electric process is carried on almost exclusively on a basic bottom. The open-hearth furnace process is carried on on a bottom which is usually quite strongly impregnated with oxide of iron, and that oxide of iron is more or less being taken up by the steel all the time. This basic hearth, or the hearth of the open-hearth furnace, may be very much more impregnated with oxide of iron some times than at other times. In the open-hearth process the melters know that the first heat on a new bottom acts differently from later heats. It acts like crucible steel lying dead in the furnace. So when we compare these three processes we must bear in mind the different hearths on which they are melted and also the different variations of each hearth in each process. If a man is to make tool steel in an open-hearth furnace—and pretty good steel can be made in that furnace—he must have the bottom free and clear as possible from oxide.

Another thing which must be borne in mind in connection with the open-hearth furnace is that we must look out for what is

known as the "old iron" which accumulates in the bottom, and if some of the old iron comes out in the bath at the latter end of the charge it will interfere with making a high grade of steel. That is one thing to be looked for in comparing the three processes. As a result of the conditions as to hearth, the open-hearth and crucible steel should be cast without delay when ready, while the electric furnace charge may be held if desired without rapid change.

WILLIAM D. MAINWARING: Inasmuch as the open-hearth has been introduced again, there is one thing which I think should be mentioned and which I think should be taken into consideration, and that is the oxidizing influence of the ore. A great many melters use too much ore in oxidizing carbon. They do not take in consideration the lapse of time between the last addition and the tapping time. If your tapping time is too near the last addition of the ore, you get too high a state of oxidation. If you have too high a state of oxidation, you have slag inclusions. If, on the other hand, you increase the lapse of time between your last addition of oxides or ore and your tapping time, you give more chance for your oxide to separate out of the bath. That is one great trouble which steel melters are having today. I only discovered this fact after going through my father's notebook, which he started down South, in Chattanooga. I have made an extended study of that factor since the first of the year.

A. H. COWLES: I want to call attention to the point of the rare elements being reduced in the electric furnace and passing into the steel, thus preventing the oxidizing of steel from the electric furnace, and, by combining with gaseous elements, producing the same effect as if you added a small amount of aluminium to open-hearth steel or crucible steel, and effecting an elimination of the gases which otherwise would produce blow-holes, etc., in the steel on cooling.

E. B. CLARKE (*Communicated*): I regret exceedingly that I could not be present at the meeting of the Society to present my remarks in person and to take part in the discussion. I note by the reports of the meeting that some exception was taken to the tenor of my remarks. For instance, I fear that

Mr. Humbert felt I had been unfair to the sellers of electric furnaces. My only answer to that would be that I did not, and do not, include *all* sellers of electric furnaces. It is perfectly true, however, that misleading statements have been made by some men interested in selling electric furnaces. Claims for power consumption and other costs of operation have been made which I feel convinced cannot be realized in practice. When power consumption of less than 600 kw. hours per ton from cold metal is "guaranteed," it should be stated that the steel produced under such conditions will probably be useless for pouring into small castings. Low "guarantees" are valueless and misleading unless the limitations surrounding their possible fulfillment are clearly stated. The same is true as to electrode consumption and lining repairs. Under peculiarly favorable conditions exceptionally good performance may be obtained, but to lead a foundryman to believe that these favorable conditions are the rule rather than the exception is wrong. Some sellers of electric furnaces are careful as to their statements. It is merely doing justice to those who only make careful statements, as well as protecting the foundry interest, to call attention to misleading statements. Those who, in selling electric furnaces, are making true statements and avoiding extravagant claims are assisted rather than injured by my remarks.

My paper was written by request to promote discussion. It was not intended to condemn electric furnaces. I am an enthusiastic believer in this method of producing high-grade steel, but it does not help matters to overlook the difficulties of the process. I maintain that experience is an absolutely essential element to success with the electric furnace. With a good furnace, properly operated by an experienced organization, steel may be produced unexcelled and, probably, unequalled by steel made by any other process.

A paper read at a meeting of the New York Section, November 20, 1913, in joint session with the Am. Inst. of Mining Engineers, and called up for discussion at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

IMPROVEMENTS IN THE METALLURGY OF ZINC.

By G. C. Stone.

It is frequently stated that there has been no change in the metallurgy of zinc since the first Belgian furnaces were built, in the early part of the last century. It is true there have been no such spectacular and radical changes as were caused in the metallurgy of iron and copper by the introduction of converters, but, in the essentials, I believe the progress in zinc metallurgy has been as great as in that of the other common metals.

The main reason that there have not been revolutionary changes is that the chemistry of zinc differs radically from that of the other metals, and these differences control the type of apparatus that can be used. The differences are:

1st. The temperature at which zinc is reduced by carbon is much above the volatilization point of the metal, and it is therefore always produced as a vapor.

2d. To obtain a merchantable product the vapor must be condensed at a temperature well above the melting point of the metal. More than this, the temperature necessary to condense zinc depends on the concentration of the vapor, and is lower the more dilute the vapor. When the mixture of zinc vapor and gases enters the condenser it is rich in zinc, and the condensation temperature must therefore be high in order to prevent sudden solidification and the production of blue powder. As the vapor leaves the condenser it is very dilute, and unless the condenser temperature is much lower there will be a loss of zinc. This means that the temperature of the condenser must be close to the boiling point of zinc (920°) nearest to the retort and very much lower at the opposite end.

3d. The reaction by which most metals are obtained commercially is

$$RO + CO = R + CO_2.$$

With all the common metals but zinc this reaction is reversed only when there is a considerable change in temperature or a very large increase in the concentration of CO_2 in the gas mixture. Neither of these is quite true of zinc. For any given temperature the equilibrium between CO_2 and zinc vapor determines the amount of reaction. That is, the reduction of zinc proceeds until there is a certain ratio of CO_2 to zinc in the atmosphere, and then stops. A decrease in the CO_2 causes the reaction to start again in the same direction, and an increase causes it to start in the opposite direction. The lower the temperature the less CO_2 it requires to reverse the reaction. In order to effect complete reduction this equilibrium must be continually destroyed by the presence of an excess of carbon, and the equation must be either

$$ZnO + C = Zn + CO$$

$$\text{or} \quad ZnO + C + CO = Zn + 2CO$$

These three essential facts limit the possible apparatus for the production of zinc in several ways. The reduction must take place in a closed chamber to prevent the loss of volatilized zinc. As the reoxidation is proportional to the total CO_2 present, and not to its concentration, and as the difficulty of proper condensation increases very rapidly with dilution of the zinc vapor, the volume of gas going off with the zinc must be kept as small as possible. This means that the gases from the heating fuel must not come in contact with the charge, or, in other words, the heating must be external. As the mixture of ore and coal forming the charge is a poor conductor of heat, the size of the chamber containing it must be small in at least one direction, or the heating will be too slow. The charge must, at all stages, contain a large excess of carbon to at once reduce all CO_2 formed. The condensers should be as close to the charge as possible and as small as will do the work in order to make it possible to maintain the proper heat gradient in them. The condensers must be kept within proper limits of temperature, diminishing towards the exit.

The first spelter furnaces built filled these conditions, and it is difficult to conceive of any other type that will do so.

It is commonly stated that the spelter furnace is very extravagant in heat. This I venture to question. Any furnace in which the issuing gases heat the incoming charge and thereby economize fuel is out of the question for reasons already given. It is therefore necessary to introduce cold charge in the furnace and heat it there. The heat used for this purpose is certainly not wasted. The heat escaping to the stack is not a large proportion of the total in a properly designed regenerative furnace supplied with gas of good quality, especially if waste heat boilers are placed between the furnace and stack. The main unavoidable loss of heat is by radiation. The end walls of the furnace are usually made very thick, and the radiation from them is not great. The radiation from the roof is much greater and is often excessive, as the roofs are usually thin. A great part of this loss can be prevented by covering the roof with a thick layer of porous material such as well-burned boiler ashes. The main radiation is from the front of the furnace, and this is necessarily so, as the front must be made thin in order to keep the retorts hot to the ends; otherwise there would be a considerable amount of unworked charge left in the front. But is this large radiation all loss? Considered only in relation to the heat required for reduction, yes; but considered in relation to the heat required for the entire operation, no. This heat is only sufficient, and not always sufficient, to keep the condensers up to the proper temperature, and it should therefore not be considered as lost, as heat from some other source would have to be supplied to the condensers if this were not available. This radiated heat regularly and automatically keeps the condensers at a suitably graded temperature, which would be difficult to do if they were heated in any other manner.

Remembering the limits imposed by the chemical properties of zinc, let us examine the progress that has been made.

Forty or fifty years ago the typical Belgian furnace contained from fifty to ninety retorts of about 0.8 cubic foot capacity each. At the present time the furnaces used in the natural gas field contain from 500 to 700 retorts of about 1.4 feet each, an increase in capacity of about 1,300 percent. Furnaces containing 1,008

retorts are in operation doing satisfactory work; this is an increase of about 2,400 percent in size and capacity. The increase in capacity of the spelter furnaces is therefore about the same as that of the modern coke furnace making pig-iron over the old charcoal furnaces.

Mere increase in size, however, does not amount to much unless accompanied by increased efficiency. In this respect the zinc furnaces show well. In the iron furnaces there has been no improvement in the proportion of metal recovered, the old furnaces having given almost theoretical results. With zinc the improvement has been very marked. In 1844 at the Vieille Montagne works the recovery was about 62 percent, and even as late as 1880, 75 percent was considered good work. Today 87 percent is only fair, and many works can show runs of long periods averaging 90 percent and over.

The fuel consumption has been decreased largely, mainly by the adoption of regenerative gas-firing. Even in direct-fired furnaces the decrease is large. Comparing only furnaces using the same kind of coal—where the hand-fired furnaces twenty-five years ago required 3, 3½ and even 4 tons of coal per ton of ore, well-equipped gas furnaces using the same coal and working the same class of ore now take only 1½ to 1¾ tons.

Labor has also been largely reduced. The old Belgian furnaces required five days' labor per charge, two men working twenty-four hours continuously, and an extra helper on the day shift only. As these furnaces worked only about a ton of ore, they required five days' labor per ton. At present all twenty-four-hour work is done away with, and not over 1½ days' labor is required per ton.

In 1844, fifteen to twenty days was the usual life of a retort. Now good retorts made in hydraulic presses last from thirty to forty days, and, at that, more are replaced because they are filled up than because they leak.

Regarding the future, I believe progress will continue to be made, but rather on the lines of improvement in the present processes than by the adoption of radically different ones.

Three main classes of processes have been proposed, the wet, electrolytic and electrothermic.

So far none of the wet processes has proved successful. One main reason for this is the difficulty of dissolving the zinc. The most abundant ore of zinc is blende, which always contains some, and usually a large proportion, of iron. When the ore is roasted the zinc and iron combine to form zinc-ferrite, which is practically insoluble in either acids or alkalies under economic conditions. To decompose a ferrite requires a large excess of acid and long boiling. The purification of the solution is also expensive and troublesome. Many inventors have proposed to precipitate the zinc from the solution as carbonate, convert this to oxide by heating, and sell the product as a pigment. This is not possible on a commercial scale, as small amounts of basic salts are always formed, and these render the oxide of zinc made of no value as a pigment; it will not mix properly with oil, and has very little covering power. The processes that start by treating the sulphides with chlorine do not appear promising on economic or technical grounds.

Electrolytic zinc of excellent quality has been made by one firm for several years, but it has never increased its original plant. It is generally believed that this plant is only possible in connection with other operations carried on by them. As a general proposition electrolytic processes have the same disadvantages as the wet, in the difficulty of making and purifying the solutions, and the added one of large power requirements. The minimum power necessary to precipitate zinc electrolytically is known, and a simple calculation will show that the amount required will cost more than coal smelting at any location in this country where zinc ore occurs in quantity.

In this country, at least, ores and coal do not occur near each other, and water power is seldom available. Therefore, power is expensive at the mine, and the freight rates on ore to points where power is cheap are high. The result is the same whether the ore is treated at the mines or brought to the power; cheap ore and power are not available at the same point. This very seriously limits the economical possibilities of electric smelting. The lowest estimate I have seen of the power requirements is 1,200 kw. hours per ton of ore, which means that power must not cost over ½ cent per kw. hour if it is to compete with the present smelting processes.

So far the yields of merchantable spelter reported as made in electric furnaces have been very low. This is not at all surprising, and is, I believe, due partly to the difficulty of properly regulating the temperature of the condensers, but more to the reoxidation of the zinc by the CO_2 in the gas forming an excessive quantity of flue dust or blue powder, which has to be reworked. That there is likely to be a much greater reoxidation in most of the electric furnaces that have been described in print than in the ordinary retort is obvious. The reactions by which zinc is reduced are the same whether the heating is by electricity or fuel:

$$ZnO + CO = Zn + CO_2$$

and $$CO_2 + C = 2CO$$

In the body of the charge the two reactions take place at the same time, and the excess C destroys the equilibrium, and there is no reversal. At the surface of the charge only the first takes place, and the CO_2 formed there goes forward and oxidizes part of the zinc in the condenser. In the long, narrow zinc retort, packed full of charge, the ratio of the exposed surface to the total volume of the charge is very small, and only a small amount of CO_2 is formed. In most of the electric furnaces of which I have seen drawings the ratio of surface to volume of charge is much greater, and more CO_2 will go to the condenser, which accounts for the greater proportion of zinc reoxidized.

In many of the electric furnaces the operation is continuous, that is, ore and fuel are charged either continuously or at short intervals. This charge of ore and coal always contains entangled air and moisture and frequently CO_2. These are rapidly driven off, and dilute the outgoing gases, making the condensation more difficult and causing a reoxidation of the zinc. It has been proposed to preheat the charge, which would decrease these troubles, but only partially, as the temperature necessary to drive off combined water and CO_2 completely and in a reasonable time is as high as the reduction temperature of ZnO.

This is confirmed by the fact that, other things being equal, a tightly charged retort will give a smaller proportion of blue powder than one loosely charged and therefore having a greater ratio of surface to volume, also that, with the Silesian practice,

where the free surface is very large per unit of charge, a larger proportion of blue powder is made than with the Belgian practice, where it is much smaller.

To be economical, electric furnaces must be in much larger units than zinc retorts, and the condensers must also be larger. It is obvious that the difficulty of keeping all parts of a condenser within the narrow limits of temperature allowable will increase very rapidly as its size increases. Increased size of furnace, which is necessary for low power consumption, therefore means an increased difficulty in condensation, and, even with the small furnaces so far built, this difficulty has been one of the most serious that has been met.

The present types of furnaces can be much improved. Fuel can be saved by better design and proportions of regenerators; better arrangement of the ports and decreasing radiation losses by more thorough lagging of the parts of the furnaces from which radiation is purely wasteful. A determination of the best size and shape of retort and condenser for different ores, and the choice of such as suit the particular ore to be worked instead of using one size and arrangement for all, will give improved results in recovery and output. A careful study and application of the principles on which ores should be mixed offer a wide field for improvement.

There have been a number of furnaces patented for the production of zinc. Several of these are on the general lines of the present furnaces, and many of them show probabilities of being advantageous. Many others are shaft furnaces, some heated by coal and some electrically. Nearly all of these have the peculiarity of requiring the zinc vapor to go in one direction and the gases in another, which is obviously impossible of accomplishment. The coal-fired furnaces of this type have the additional disadvantage of producing a large volume of gas, which would much increase the amount of blue powder made and the difficulty of condensation.

In the old days metallurgy was purely empirical, and progress was slow in all lines. Iron and steel were the first to be taken up by trained men, and the results they obtained were startling and revolutionary. Copper and lead followed next, with equally beneficial results. Zinc was about the last to employ trained

metallurgists, but they have taken hold of it at last, and I have sufficient confidence in them to believe they will continue to improve on the good work they have already done.

A paper read at a meeting of the New York Section, November 20, 1913, in joint session with the Am. Inst. of Mining Engineers, and called up for discussion at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16-18, 1914.

ELECTRIC ZINC SMELTING.

By W. R. Ingalls.

The idea of electric zinc smelting is no new thing; nor is it still merely in the laboratory stage. For several years a considerable tonnage of electrically smelted spelter has been produced commercially in Sweden and Norway. In 1911 there was a production there of 6,575 long tons, in 1912 of 8,000 tons; in 1913 it will be larger.[1] Although I have no detailed information about this, I am under the impression that the larger part of this spelter is derived from re-smelting dross, scrap, etc. However, some of it is derived directly from ore.

I shall not go into the historical phase of this subject any more than is necessary to give a little perspective. The Cowles brothers first tried the electric smelting of zinc ore about 1884, but were diverted into the field of aluminum. DeLaval, the distinguished Swedish inventor, about 1898 took out patents on his well-known arc furnace, which is depicted in many text books, and tried it in Sweden about 1901, since which time works have been running at Sarpsborg and Trollhättan more or less continuously. Also there is a plant at Ihlen, near Trondhjem.

According to the report of the Hydraulic Power & Smelting Co. on Nov. 4, 1913, the capacity of the works at Sarpsborg had been increased from 8,000 to 10,000 tons per annum. Erection of a new zinc smelting works at Trollhättan is proceeding as rapidly as possible. At the present time, of the seventeen 1,000-hp. furnaces and eight 500-hp. furnaces to be installed, thirteen of the former and all of the latter are completed. (The 500-hp. furnace has probably a daily capacity of about four tons of ore, and the 1,000-hp. furnaces twice as much.) The company goes on to say in its report that its furnaces have been running on the ordinary classes of roasted ore, which have not yet proved

[1] Statistics published in January, 1914, give 17,000 tons for 1913.

commercially profitable. Considerable progress is, however, being made, and the results achieved in August, 1913, were a great improvement over any previous month.

Since 1901 there have been many patents taken out by many experimenters, and several ambitious experiments have been made, most of which have been disappointing. Although electric smelting has been commercially carried on in Scandinavia, the measure of its success is doubtful, and certainly metallurgical difficulties have been experienced which would prohibit the Scandinavian processes almost anywhere else. The same metallurgical difficulties have been experienced by other experimenters.

Nor shall I enter upon any remarks reviewing the deficiencies of the ordinary process of fire smelting and the hypothetical advantages of electric smelting, which have been recited as a panacea for previous ills. The ideas about smelting zinc ore in a large instead of in a small retort, of generating the heat exactly in the place where it is needed, of substituting a continuous operation for an intermittent one, are engaging, each and all of them, but let us first consider just what these ideas involve.

An early metallurgical difficulty was the proper condensation of the zinc. Spelter was wanted; blue powder was got. I use the term "spelter" as meaning zinc condensed in molten form. The condensation of the zinc as blue powder in whole or in large part was a bar to success. Until we were able to leap that hurdle there was not much use in thinking of the other obstacles. If, as at Trollhättan, it were necessary to re-smelt two tons of blue powder with every ton of ore, the energy required would be prohibitive except in places where power is available at a phenomenally low figure. Many investigators of this subject have considered the trouble in condensing the zinc vapor in the right way to be in the condensing apparatus. I shall indicate further on that the trouble really originates in the furnace itself, and is not very much a matter of the condenser; that, given the right conditions in the furnace, condensation is effected without any special difficulty. Before going further into this subject it is well to reflect upon the inherent differences of electric smelting, or what we hope to make of electric smelting, and the ordinary practice in smelting, to which, for convenience, I shall refer as fire smelting.

Fire smelting as ordinarily practised is a two-stage intermittent process. The retorts are charged and are then slowly heated. Hydrocarbons are driven off, carbonates are decomposed, and preliminary reductions are effected in the charge. During this stage the gas, high in carbon dioxide, burns with a violet flame at the end of the condenser. The second stage is the stage of zinc reduction and distillation. When it is completed the residues are discharged. The next day the same cycle of operations is repeated.

Electric smelting is aimed to be continuous, and many experimenters have contemplated doing eveything in one operation. I do not believe that to be possible. Electric smelting can be made, in fact, is made, a continuous process, but it must be a two-stage process. Either the first stage of fire smelting must be done in a separate furnace, or the charge put directly into the electric furnace will yield blue powder. The blue powder must be re-smelted in order to get spelter, so we still have a two-stage process.

Assuming a properly preheated charge, what differences are there then between the internally electrically heated retorts and the externally fire-heated retorts?

In the former there are, among other things, (1) an absence of excess of carbon in the charge, (2) the ore is dropped upon very hot slag (in the case of some furnaces, at least), (3) there is possible exposure of the charge to excessive temperature, and (4) there are possible electrical effects.

Now we know that the reaction between zinc oxide and carbon monoxide is reversible. We know that in fire-smelting, blue powder is formed, especially in the earlier part of the distillation. We know that the retort gas is then relatively high in carbon dioxide. We know that subsequently the gas becomes almost pure carbon monoxide. We know that attempts to obtain zinc from the blast furnace have given only blue powder, because of oxidation by either carbon dioxide or oxygen.

Let me digress long enough to explain the nature of blue powder. There are two kinds, viz.: meltable and non-meltable. The meltable powder results from improper physical conditions. The non-meltable results from improper chemical conditions. This substance, which between the fingers appears to be an

impalpable powder, when examined under the microscope is seen to consist of a myriad of little pellets, mostly spherical and coated more or less with some substance that prevents their coalescence. That substance may be zinc oxide, or may be something else. The pellets sometimes exhibit a frosted appearance, and sometimes show what look like minute white hairs.

In the metallurgical treatises, blue powder condensation is commonly ascribed to the condenser being too cold. That may account for the meltable blue powder, but how can it account for the oxidation exhibited by the non-meltable? Whence comes its oxygen but from carbon dioxide? The gas from electric furnaces operated without especial precautions is invariably high in carbon dioxide. The presence of that oxidizing and diluting gas is sufficient explanation of the formation of blue powder.

Carbon dioxide is not the only source of trouble, however. The essential condition of zinc condensation is purity of the gas and vapor. Impurities may be: (1) Carbon dioxide and other gases, (2) dust, (3) substances volatile at high temperatures. A step is gained when we recognize the causes of blue powder. Recognizing them, however, the avoidance of them is not entirely easy.

I am not going to describe or discuss at this time either processes or types of furnaces. Some European experimenters have worked on the line of a preliminary pyro-metallurgical concentration and the smelting of a collected zinc oxide fume. American experimenters generally have directed their attention to the direct smelting of ore and the elimination of gangue by scorification in the electric furnace itself. Among the furnaces we have those of the arc, arc-resistance and resistance types. Patent specifications show many freakish designs. Among the furnaces seriously tried there are such as the horizontal cylinders of Queneau, Specketer and Weeks, the radiation furnaces of De Laval, and FitzGerald & Thomson, and the pot furnaces of Cote-Pierron, Salguès, Johnson and others. Reduced to their elements, there is no fundamental difference among them.

I have touched, in this discourse, only upon the high points of the subject, and have conveyed the impression, I hope, that we are very far from knowing all that we need to, even in respect to them. I shall indicate that we know still less in trying to answer the question: What warrant is there for the wide-

spread attention to electric smelting and the large sums of money that are being spent in trying it? My answer to that question is that not even yet have we much beyond visions and ideas. We have very few facts and conclusive figures. Electric smelting is one of the relatively unexplored fields of metallurgy, and is attractive because of its mystery, if nothing else. Among our visions we conceive the possibilities of smelting certain kinds of ore that are extremely troublesome or even impossible in the fire-smelting process. The range of such ores is much less today than only a few years ago, but we still find difficulties with ores containing a fluorspar gangue, with sulphide ores that are very high in isomorphous iron, and with those ores that are cryptocrystalline mixtures of component sulphides. There is, moreover, the possibility of increasing the extraction of zinc, and especially is there a possibility of increasing the extraction of the lead and silver content of zinc ore, from which our present methods secure too small a proportion, perhaps not more than five-eighths from each, if I may venture upon a generalization.

Recognizing that electric zinc smelting is a performable process, the question of importance is the economy of the process, in other words, the cost of performing it. Let me make haste to say that, in the case of those ores from which a recovery of lead and silver, besides zinc, is expected, we should make comparison with the cost of the total process as ordinarily conducted, *i. e.,* the extraction of zinc and the subsequent extraction of the lead and silver from the residuum. Unfortunately we do not yet possess the data that warrant us in coming to any firm opinion respecting the cost of electric smelting.

A crucial point is the matter of energy, which in the process of fire smelting is used in the form of coal, and in the electrical process in the form of electric current. In the smelting of 1,000 kg. of zinc ore, of about 25 to 50 percent zinc content, it is estimated that from 900 to 1,050 ton calories of heat are necessary, which is equivalent to 1,047 to 1,221 kw. hours of electric energy. In mentioning these figures, I mean, of course, to make a broad generalization, a translation of energy from terms of heat to terms electrical. If the electric smelting process be conducted as a two-stage process, where preliminary reactions are

effected in an auxiliary furnace fired with coal, as Mr. Johnson does, and this partially-reduced hot charge be delivered to the electric furnace, the power required in the latter will naturally be diminished. No doubt this is a proper direction in which to work, *i. e.,* to use the cheaper energy of coal wherever it can be used and confine the more costly electric energy to work for which it is especially needed. On the basis of an estimate of 1,200 kw. hours, it will readily be seen that, under any conditions of power supply that we know of in this country, the power cost of reducing a ton of ore will be more than the coal cost. By just so much as the use of electricity can be limited, by just so much will the balance swing in its favor.

Comparing fire smelting and electric smelting, with respect to the items of administration, general expense and yard labor, we may expect about the same costs in the one process as in the other. In the matter of roasting we may admit some economy in favor of the electric smelting process, inasmuch as the ore for that process may not have to be desulphurized so completely as in the ordinary process; indeed, we may not want to desulphurize it so completely. The consumption of reduction coal is undoubtedly in favor of the electric furnace. We can not, in the electric furnace, use the same proportion that we do in the ordinary furnace, even if we should want to. Setting the consumption of electrodes against the consumption of retorts, we can not yet safely say which will be the more costly. It has been argued at considerable length that electrodes will be very much cheaper than the retorts of the ordinary furnace. The exponents of that idea may be right. I say only that at the present time we do not know, and in the only extensive work in electric smelting that we know of, the work in Scandinavia, the cost of electrodes has been higher than the cost of retorts in the ordinary process as practised elsewhere in Europe.

The matter of labor cost is also quite uncertain. At first sight one is apt to jump to the conclusion that, in running an electric furnace of three or five tons' daily capacity, the labor cost would be much lower than in our present furnaces in which we have small retorts. That may be so; at present we only surmise. It may be overlooked that in our present furnaces the organization of labor is highly developed. The maneuver

requiring the most labor is concentrated in a few hours, and during the remainder of the 24 hours a few men attend to a big furnace comprising a great many retorts. Anyway, at Trollhättan the labor cost in 1911 was more than in ordinary fire smelting elsewhere in Europe. As to repairs and renewals in electric smelting we know next to nothing. In the matter of capital charges I think it is not unlikely that the electric plant will have a little advantage, *i. e.*, if it be not charged with the cost of electric installation, which, of course, would be improper, because that has already been reckoned in considering the cost of electric energy.

Summarizing, if the unit quantities of materials used in Sweden and Norway be multiplied by American costs, especially those of the region west of the Rocky Mountains, the total cost of the application of the process used there would be prohibitive. The whole subject of electric smelting is in its infancy. Yet it is possible that ways around some of the difficulties that we now see, including those pertaining to matters of cost, may be found, and that in the end we shall in one way or another be able to see some advantage in electric smelting. Anyway, it is a subject that is worth the work that is being put into it.

DISCUSSION.

W. McA. Johnson: I regard electric zinc smelting from a different viewpoint than that taken by Mr. Ingalls. As a critic, I believe that I have given the subject hard study. As a worker, I have done something. The result of my efforts has the finality of emphasizing the fact that the proper lines of commercial advance is availing oneself of the principle of matting and slagging, which is the inherent point of advantage that the electric furnace possesses over the retort furnace.

Add to this the fact that lead-ore and copper-ore, considered as such, require in the Johnson furnace much less power than zinc-ore, and can be smelted for a third of the cost of smelting zinc-ore, it seems to me a foregone metallurgical conclusion that the lines we have developed are precise, proper and correct. These lines are:

(A) Pre-reducing the refractory low-grade ore, which at the same time may be regarded as a high-grade ore, if total gross metal value be considered.

(B) Subsequent electric smelting whereby slag, copper-matte and base lead bullion are tapped concurrently from the furnace, and spelter from the condenser.

The question of condensation has been so long under such firm control by us that it rarely enters any discussion among our technical staff, and I thus pass it by in these remarks.

The points of proper furnacing and control of furnace, so as to make a suitable matte and slag, are more important, and well-nigh essential, and, of course, there are commercial considerations that far outweigh such engineering matters.

Energy consumption is one of these. While it is by no means impossible to design a furnace that will smelt a 30 percent charge for 600 kw. hours, there are reasons that can be adduced to show that it would not be good business to bother about this task. Mr. Ingalls' figures on page 173 are not consistent, for the difference of net heat-requirements on 25 percent zinc-ore and 50 percent zinc-ore is, according to our work, triple the 150 ton-calories, or 174 kw. hours given by him.

The question of electrode consumption is another point. Our tests show that it is possible to make this consumption anything from 2 lb. to 30 lb. per ton of ore. At all events, this is another matter of the "business equation."

We do not criticise Mr. Ingalls unduly, but his statement about labor cost of electric zinc smelting undoubtedly gives a wrong impression.

Using the analogy of history, we would reason as follows:

(1) All metallurgical operations when conducted in increasingly large units have a decreasing labor cost per ton of material treated.

(2) Electric zinc smelting when properly carried on is a metallurgical operation that can be conducted in large units.

(3) Electric zinc smelting will have a decreasingly small labor charge per ton of material treated, provided intelligence and skill are employed.

This is what the modern metallurgy of lead, copper, iron and steel teaches.

Looking at the question of labor cost from another standpoint, we can say that a 100-ton coal retort plant needs about 250 men exclusive of the roasting gang. I have completed the plans of a 10-ton unit, and I am designing a 100-ton plant. I am unable to see where 250 men could be employed on such a 100-ton unit unless a grandstand was erected so as to provide room for them to sit down.

Mr. Ingalls' term "fire-smelting" is not as good a term as "retorting." Zinc-ore in the retort is not "smelted"; in fact, in the United States any fusion is carefully avoided. The use of the term "retorting" is sanctioned by many practical zinc men, and it is better than "fire-smelting."

In present retorting practice, where lead values are important, the "retort-residues" are scraped out, and not "blown out." The handling of these residues has caused many workmen to be "leaded," or poisoned by lead. One of the marked advantages of the Johnson process is the avoidance of this intermediate step, which is liable to be so injurious to the health of the workman; the electric furnace yields base bullion direct.

Considered in a general way, Mr. Ingalls' paper is a fair presentation of the state of the art, so far as it has been published. Experience of life teaches me to have an increasing respect for facts—mental, moral and physical facts, and for truth. There is much of truth in Mr. Ingalls' article, and many physical facts are well stated. I understand his point of view and appreciate it.

W. R. Ingalls: The energy required to reduce the zinc oxide of an ore is proportional to the percentage thereof, but as the zinc content goes down, other work that must be done goes up. Consequently there is less difference in the energy required for a 25 percent and a 50 percent ore than might be supposed. This not only is in conformity with theory, but also with the results of practice.

My remarks about labor cost were based on consideration of the experience so far. Mr. Stone, in a paper presented at the same time as mine, generalized the requirement in our existing

furnaces as "not over 1½ days' labor" per ton of ore. We shall best postpone figuring on the crew of a 100-ton electric furnace until somebody has built and operated such a one, and is not merely imagining it. We are far from knowing that the operation of such a furnace is practicable.

To those who object to my simple, distinguishing term, "fire smelting," I will acquiesce when the term zinc smelting be abolished and all of our zinc smelters become "zinc retorters." I am unaware that any lexicographer defines smelting as a process of complete fusion, or that the raking-out of the non-liquified "gray slag" of the Scotch hearth and Flintshire furnaces has caused the reduction of lead ore in those furnaces to be called anything but lead smelting.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 16, 1914.

ADVANTAGES OF SOUTH-EASTERN ALASKA FOR HYDRO-ELECTROCHEMICAL INDUSTRIES

By W. P. Lass.

Much has been said of the resources of Alaska, the rich placer deposits of the interior, the vast coal and copper deposits to the westward, the large low-grade gold deposits in the vicinity of Juneau and the extensive timber lands in southeastern Alaska, but little has been said of the water-powers of southeastern Alaska that are yearly consuming their own energies as they are allowed to run undeveloped, while "millions of dollars are being expended in other countries for hydro-electrochemical industries."

The object of this paper is to call attention to the natural resources of southeastern Alaska for industrial and manufacturing purposes, whose utilization is made possible by cheap hydro-electric power, also to give some idea of the investment required, manufacturing costs, markets and profits.

The greater part of southeastern Alaska, although undeveloped, unsurveyed and unprospected, has been held in national forest reserves, and little attention paid by any one to its development and utilization. It has not been an easy matter for the average layman to determine the conditions under which he may obtain title to a particular piece of property, whether it be coal, timber, water rights, manufacturing site or agricultural ground. As a result of this policy of inaction the country has lain dormant, awaiting the attitude of the government in the disposal of these rights. Whether conservation means public ownership privately operated, or corporate ownership operated under government supervision, has not been so important to the welfare of Alaska as the establishment of some fixed policy by the government under which parties could develop the natural resources, and laws under which the prospector would be assured of the support of his government. The present generation has

the ability and should have the right to use efficiently the great and abundant water-power resources of Alaska that are not limited in quantity or, like mines, contain but one supply. They are an ever-flowing source of power that lost today can never be regained.

"No other country in the world is more amply provided by nature with resources that make for national greatness." It is to the future of Alaska that her inhabitants look.

During recent years there has been a notable awakening in the attitude of the federal government regarding the development of these resources, and its attitude is now very clearly defined in the National Forest Manual issued by the Department of Agriculture, which went into effect February 24, 1913; the keynote of this manual is development under governmental supervision, that exploration and exploitation must be followed by development to highest utilization. Title to water rights in perpetuity can no longer be obtained, but permits for the use of the water for fifty years, subject to renewal, may be obtained by the payment of nominal fees not exceeding one dollar per H.P. year.

This policy of rental of the national resources also serves as a protection against would-be trespassers; government rental spells government protection, and as this policy of the government becomes more definitely known it is believed it will meet with great favor and do much to aid the development of the water powers of Alaska.

Many well-informed people consider the whole of Alaska a region of perils and privations, shut off from all communication with the outside world for six months of the year. While this may be true of the region lying within the Arctic Circle, it is not the case with southeastern Alaska, a small section of the whole territory, yet containing more than half of the whole population of Alaska.

Alaska is contained within the same degrees of latitude as the Scandinavian Peninsula. Southeastern Alaska is in the same latitude as the British Isles, and warmed by the Japan stream, enjoys much the same climatic conditions as Scotland; Ketchikan is no farther north than Glasgow or Copenhagen. Southeastern Alaska enjoys more moderate winters than either New York or Chicago, as is shown by the reports of the U. S. Geological Sur-

vey. This section of the country is subject to abnormal precipitations. The maximum amount of rain falling in 24 hours varies from 3 to 7 inches. The daily mean temperature and precipitation of various points from 53 degrees to 61 degrees north latitude are to be found in the condensed meteorological reports made public in the Annual Report of 1912 of the Alaska Experimental Station, in charge of C. C. Georgeson, special agent for the United States Department of Agriculture.

Southeastern Alaska is interlaced by a network of navigable bays, inlets and fiords whose shores rise precipitately to an altitude of two or three thousand feet. The traveler along the Inside Passage has always been impressed by the many beautiful waterfalls, the thousand of islands, the mountains rising abruptly from the water, and the many glaciers along the summits. From Dixons Entrance to Mt. St. Elias there is not a section of the country more than forty miles from salt water.

The boundary line between Southeastern Alaska and British Columbia is on an average about 30 miles from salt water, and has an average elevation of about 5,000 feet. This high altitude, covered with perpetual snow and glaciers, serves to intercept the moist winds from the Pacific Ocean, causing an extremely heavy precipitation.

Lakes situated high up in the mountains at altitudes of 1,000 feet or more above the sea and having narrow outlets through rock gorges can be found, and afford an easy means of conserving the precipitation and equalizing the flow throughout the year. There are no records to show just what this precipitation amounts to over these areas of high elevation. Government records of precipitation for southeastern Alaska are all taken near sea level. Measurement of stream flows from definite drainage areas indicate an average precipitation 100 percent greater over the drainage areas than the precipitation recorded at tide water.

This greater precipitation is accounted for by the decrease in temperature at higher altitudes, which in the vicinity of Juneau is 1½ to 2 degrees F. for a 100 foot rise in elevation (2.7 to 3.7° C. per 100 meters), and further by the rugged character of the topography and by the glaciers which completely cover the backbone of the coast range.

It is the opinion of the writer, who has lived in southeastern

Alaska for the past seven years, that this territory offers a most attractive field for the establishment of hydro-electrochemical industries, or other industries demanding cheap power and an accessible market.

In order to successfully undertake any large electrochemical industry it is of prime importance to have a large amount of cheap power.

An investigation of the precipitation records for southeastern Alaska as published by the government, and inspection of contour maps of this section of the country, will convince the most skeptical of the abundant water-power resources of southeastern Alaska.

At the present time only a very few of the available water powers have been developed. These are mainly adjacent to the cities and mines, where a limited amount of power is used. Many of the more favorable sites are at a considerable distance from centers of population or industrial activity, and could be made available only by establishing the industry at the site of the power. Furthermore the deep fiords and rugged character of the country make long transmission difficult and expensive.

One of these power sites which has been investigated is the Speel River Project, situated about 40 miles southeast of Juneau. From the report of E. P. Kennedy, Assistant Superintendent of the Treadwell Mines, the amount of all-year power that may be economically developed from the vicinity of Speel River, Alaska, is in the neighborhood of 100,000 H. P. Mr. Kennedy estimates the cost of generating electric power at Speel River, allowing 10 percent for interest and depreciation, will not exceed five dollars per H. P. year. It is believed that this development is but one of many possible hydroelectric developments that may be installed for a capital expenditure of less than $50 per H. P.

Another essential to the establishment of hydro-electrochemical industries is accessibility to market.

The entire country is open to navigation at all times of the year, either from the open ocean or from the protected Inside Passage. The regular fare, first class, from Seattle to Juneau, the capital of Alaska, is $25, which includes berth and meals. The freight rate has varied from $2 per ton on ore shipments to $4 and $6 per ton for merchandise. Very attractive rates could

no doubt be obtained from the steamship companies desiring a return cargo for their steamers. Such locations would permit shipments to be made by barges to Puget Sound and San Francisco or by boat to any foreign port.

There are economic deposits of pure limestone, marble, gypsum, silica and pyrites in southeastern Alaska lying exposed at the water's edge. The Bering River and Matanuska coal field to the westward contain high-grade semi-bituminous and anthracite coal, as well as producing oil wells and a refinery supplying the local demand for distillates. The crude California oil with an asphaltum base may be obtained for $1 per bbl. This oil would be suitable for the manufacture of the electrodes used in electric furnaces. The above are the more essential materials used in electrochemical industries.

The Gold Mining Companies in the vicinity of Juneau are daily throwing away 100 tons of iron pyrites, carrying 38 percent sulphur and 40 percent iron. These concentrates contain no impurities detrimental to the iron and steel industry. It is quite probable that in the near future a far greater tonnage of sulphide ores will be for sale in the vicinity of Juneau. Some of these sulphides contain considerable quantities of both zinc and lead, and could be treated to advantage in electric furnaces, recovering not only the sulphur, but lead and zinc, both of which would find a ready market in the West. At the present time there are no zinc smelters west of Colorado, and owners of low grade zinc-lead ores on the Pacific Coast are usually penalized for their zinc.

There are known deposits of iron ores in Alaska. The production of pig iron and steel has been out of the question on the Pacific Coast due to the poor quality and high price for coal and coke. The opening of the Matanuska coal fields will supply this demand for a high-grade coking coal. One H. P. year will produce approximately 3 tons of pig iron. The factor governing the economic success of an electric pig-iron furnace is the comparative cost of a specific number of calories of heat obtained from coal or from the electric current. When one horse-power-year can be produced more cheaply than the cost of two tons of coal, it is commercially practical to substitute electric heat for carbon heat.

Coke is not a suitable material for reduction purposes in electric

shaft furnaces on account of its electrical conducting properties. Thus electric steel furnaces are most desirable where an abundance of charcoal may be obtained together with cheap power.

By the use of Herreshoff burners, one ton of pyrites will produce 2 tons of concentrated sulphuric acid. The cost of producing 50° B. acid in Alaska has been estimated at $2 per ton. This acid is the basis of all chemical industries and would be used in the manufacture of wood-pulp and paper, or combined with phosphates to make fertilizers. Sulphuric acid is largely used in the manufacture of blasting powder, some powder requiring as much as 50 percent of its weight of acid. The gold mines in the vicinity of Juneau purchase annually 2,000,000 pounds of blasting powder. The demand for powder may be expected to increase when the railroads begin construction work and the large low-grade mines become developed.

At present most of the powder manufactured in the United States contains nitrates imported from Chile, while the whole industry could be carried on in Alaska where nitric and sulphuric acid as well as the absorbants could be readily obtained. Thus we come to the fixation of atmospheric nitrogen, which in Norway has proved to be a highly profitable industry.

It is believed that the Alaska coast offers the same advantages as Norway for the establishment of electrochemical industries, with the exception of the cost of labor, which is $3 to $4 per day. However, in the manufacture of air nitrates, very few men are required; a furnace consuming several thousand kw. requiring only part of the time of one attendant.

The chief problem in the manufacture of air nitrates is not the production of pure nitrogen but the production of nitrogen compounds such as nitric acid, sodium nitrate, calcium nitrate and ammonia.

One kw. year will produce a half ton of nitric acid by either the Pauling or Birkeland & Eyde electric furnaces. This acid would have a market value of 3 cents per pound.

Among the supplies of greatest interest to the gold mines of the West are cyanide and powder. At the present time cyanide can be imported from London and sold in Seattle or Juneau for the same price as our home product, which has to be obtained from New York. The demand for cyanide will increase as the

LEGEND
Gold placers
Gold and silver lode mines and prospects
Copper mines and prospects
Coal-bearing rocks
Areas known to contain workable coals
Anthracite semianthracite and semibituminous, including the better coking coals
Bituminous and subbituminous coals
Lignite
Petroleum seepages
Marble and gypsum deposits
INDUSTRIAL MAP
OF
SOUTHERN AND SOUTHEASTERN
ALASKA
SHOWING NATURAL RESOURCES AVAILABLE FOR
HYDRO-ELECTRO-CHEMICAL INDUSTRIES.
Scale
Compiled for W P Lass
Ft. Yukon
Eagle
Fortymile
Dawson
Yukon
Circle
Fairbanks
Tanana
Yukon River
Selkirk
Lewes River
Teslin River
Whitehorse
Atlin
Boundary Line
Yukon District Alaska
Yukon District British Columbia
Klaune L.
Shagway
Coast Range Mts.
Juneau
Muir Glacier
Johns Hopkins Glacier
Admiralty I.
Chichagof I.
Kupreanof I.
Baranof Id.
Prince of Wales I.
Wrangell
Revillagigedo I.
Tongass
Dixon Entrance
Iphigenia Bay
Mt. McKinley
Chugach Mountains
Valdez
Copper River
Bering River Coal Field
Bering Glacier
Katalla
Controller Bay
C. St. Elias
Matanuska Coal Fields
Prince William Sound
Hope
Kenai
Kenai Peninsula
Cook Inlet
Gulf of Alaska
Pacific Ocean

Record of Total Precipitation (in Inches.)

Month	Precipitation for 1912								Mean for 5 yrs.	Mean for 17 yrs.
	Calder	Fortman Salmon Hatchery	Ketchikan	Juneau	Sitka	Cordova	Seward	Valdez	Juneau	Sitka
January	5.55	8.26	.....	0.54	3.18	.....	9.00	3.04	10.61	12.17
February	11.85	13.93	.....	7.16	5.90	.....	.....	4.97	4.85	7.47
March	3.30	4.41	.....	2.72	5.01	16.79	5.77	10.97	6.62	6.70
April	6.25	8.55	.....	2.93	2.67	4.02	4.29	0.71	5.25	5.61
May	6.00	6.01	7.15	4.26	3.66	20.29	8.39	5.45	7.36	4.11
June	6.00	7.53	6.65	5.53	3.49	5.66	0.53	1.23	4.99	3.31
July	3.55	4.91	5.60	3.60	3.84	4.99	3.10	5.10	5.59	3.55
August	4.01	5.38	4.89	6.50	9.07	23.16	13.04	7.05	7.53	5.84
September	9.80	11.89	16.44	9.60	8.27	49.63	13.91	18.74	12.19	9.67
October	21.55	21.23	27.78	14.80	15.13	24.88	9.29	6.99	10.05	11.96
November	14.85	20.59	18.47	7.94	9.92	5.73	9.84	2.47	10.47	9.80
December	19.12	19.19	21.23	13.25	19.87	13.47	9.89	9.14	8.16	7.88
Yearly Total	111.83	131.88	108.21	78.83	90.01	168.62	87.05	75.86	93.67	88.07

price is lowered; for instance, if the Treadwell Company were to cyanide their tailings the cost for cyanide at its present rate would be $164,000 yearly. This cyanide could be manufactured in Alaska for half of the above cost. With the price of cyanide reduced, treatment of low grade ores becomes more profitable.

Five thousand horse-power of electric energy could be commercially utilized by the establishment of a wood pulp industry. Such a plant requires large quantities of clear water, which is here available free from damage suits for stream pollution. For such an industry Alaska offers abundant timber, with adjoining water powers and sulphur deposits.

Investigations conducted during the summer of 1913 by the U. S. Bureau of Soils, looking to the possibility of the utilization of the kelp of the Pacific Ocean as an economic source of potash and other products, establishes the fact that the giant kelp of Alaska waters known as *nereocystis* is as available a source of potash salts as that of the more southern waters. Ashes of samples taken from southeastern Alaska waters contained from 20 to 25 percent K_2O and over 50 percent of their weight soluble salt. This kelp could be economically dried by the waste heat from electric furnaces.

It is believed the location and natural resources of southeastern Alaska are such as to invite development for electrochemical and industrial purposes, and that, given proper governmental support, Southeastern Alaska will be converted into thriving industrial communities, more valuable to her than either her gold mines or her fisheries.

SITKA—THE FORMER CAPITAL OF ALASKA.

JUNEAU—THE PRESENT CAPITAL OF ALASKA.
Treadwell Mines in the Distance.

SPEEL RIVER PROJECT—TEASE LAKE.
Elevation above Sea Level, 1010 ft. (310 m.). Distance from Tidewater 4000 ft. (1.2 km.).
Average Yearly Flow, 224 cu. ft. (6.4 cu. m.) per second.

SPEEL RIVER PROJECT—CRATER LAKE AND OUTLET.
Elevation above Sea Level, 946 ft. (287 m.). Distance from Tidewater, 5000 ft. (1.5 km.).
Average Yearly Flow, 299 cu. ft. (8.6 cu. m.) per second.

SPEEL RIVER PROJECT—LOOKING UP LONG LAKE.
Elevation above Sea Level, 727 ft. (220 m.). Distance from Tidewater 10,000 ft. (3 km.).
Average Yearly Flow, 746 cu. ft. (21.3 cu. m.) per second.

A lecture delivered by invitation at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914, President E. F. Roeber in the Chair.

LEACHING AND ELECTROLYTIC TREATMENT OF COPPER ORES AT CHUQUICAMATA, CHILE.

By E. A. Cappelen Smith.

The Chuquicamata copper mine, of the Chile Exploration Company, is located at Chuquicamata, a station on a branch of the Antofagasta and Bolivia Railroad, in the Province of Antofagasta, Chile, between 22° and 23° south latitude. Chuquicamata is 165 miles (275 km.) by railroad from Antofagasta, and 82 miles (135 km.) in a straight line from the coast, and lies at an altitude of 9,500 feet (2,850 m.) above sea level.

The deposit has long been known as the Atacamite deposits of Chile, and for many years past has been mined by the natives. As evidence of their operations we find in the old workings many stone utensils—hammers, etc.—and mummies.

The deposit is a brochantite mineral contained in the cleavages of the granodiorite, mixed in part with chalcanthite and to some extent with atacamite, and with a deposit of salt. A small amount of caliche containing nitrates is also present in the upper layers of the ore body.

The so-called Llampera ore body extends for a distance of approximately 8,000 feet (2.4 km.), with an average width of about 500 feet (150 m.). Throughout the whole length of the deposit numerous tunnels have been run, and a very large quantity of ore has been left on the dumps from these tunnels. From the tunnels raises have been made almost to the surface, leaving in places a shell over the workings 8 to 12 inches (20 to 30 cm.) thick.

A few shafts have also been sunk in the ore deposits, the deepest one to a depth of 110 meters.

The property was acquired by Mr. Albert C. Burrage, of Boston, who, in connection with the firm of Messrs. M. Guggenheim's Sons, formed the Chile Exploration Company, which company now owns the property.

The property has been explored by churn hole drilling. The drilling has developed an ore body in excess of two hundred million tons. Most of the drill holes, however, were stopped while the bottom of the hole was still in ore.

The general direction of the ore body is north and south. Lately a number of drill holes have been sunk at a considerable distance west of the Llampera, and, after going through from 300 to 400 feet (90 to 120 m.) of capping, chalcocite and chalcopyrite have been encountered, giving indications of a very materially increased tonnage over that reported up to date.

In the Llampera zone, of the two hundred million tons of ore so far developed, approximately two-thirds are brochantite and one-third sulphides.

No change in the formation has been shown, even in the deepest drill holes, the ore still appearing to be in the cleavages of the granite. The lower drill holes show primary ore.

From the amount of ore developed and indicated it appears that the Chuquicamata mine is probably the largest copper deposit known today.

It was generally assumed that this large and well-known deposit of ore was atacamite, and as such could not be treated at a profit by any of the established methods, first, on account of the highly siliceous nature of the ore and the absence of sulphides and water, and, second, on account of the volatilization in smelting of the copper chloride.

It was demonstrated that the mineral was not atacamite (oxychloride), but brochantite (oxy-sulphate), and that mixed with the brochantite in the upper parts of the ore body was a deposit of salt. The brochantite, being an oxy-sulphate of copper, is insoluble in water, but very readily soluble in dilute sulphuric acid. It was therefore evident that the way to treat the brochantite ore body would be by wet methods.

PRELIMINARY EXPERIMENTS.

About six hundred tons of the oxidized ore, representing, as near as we can judge, a fair average of the oxidized ore body, have been shipped to New York for experimentation on a small scale.

In addition to this shipment, more than 2,000 composite samples representing every 25 feet drilled in each drill-hole have been sent to New York. Leaching tests and complete analyses have been made in order to determine if the oxidized ore body as a whole, as developed by the drill-holes, is similar to the 600-ton shipment.

The results of all of these leaching tests and analyses prove that we are justified in expecting equally good results on the whole oxidized ore body as those which we have obtained while treating the 600 tons; in fact, the average impurities contained in the whole ore body, such as chlorine, nitric acid, soluble iron, etc., are very considerably less than contained in the 600-ton shipment.

At first, tests were run on a very small scale, and gradually—as promising results were obtained—on a somewhat larger scale, treating about two tons of ore per day. The average content of the ore thus treated was somewhat in excess of 2 percent in copper.

The main problems which presented themselves for solution were:

1. The solubility of the copper minerals in sulphuric acid.
2. The amount of chemicals required as a solvent.
3. The amount of impurities which would enter the solutions.
4. The precipitation of the copper from the solutions obtained.

The principal developments in the solving of these problems may be briefly summarized as follows:

1. *Solubility of the Mineral.*—Experiments conducted on a small scale disclosed the fact that the copper-bearing mineral was very readily soluble in a cold dilute sulphuric acid solution, and that only, comparatively speaking, coarse crushing would be required.

2. *Chemicals Required.*—After prolonged experimentation it was found that the ore yielded enough sulphuric acid, from the decomposition of the copper sulphate present in the brochantite, to more than make up the losses in sulphuric acid in the operation. The losses of acid occur mainly in two stages—first, the loss

due to dissolving other components besides copper from the ore, and, second, due to wasting of solutions through discarding of the residues.

3. *Impurities Entering the Solutions.*—Experimentation extending over a long period of time has shown that no deleterious amount of impurities will accumulate in the solution, other than the chlorine derived from the salt deposit mixed with the mineral in the upper parts of the ore body.

4. *Precipitation of the Copper.*—The experiments conducted in our experimental plant have shown conclusively that electrolytic copper of the highest grade can be produced from the sulphuric acid solutions obtained.

EXPERIMENTAL LEACHING.

After completing a number of leaching tests on a laboratory scale, and after running a number of tests each with 100 kilos of material, experimentation was inaugurated on a larger scale, and a plant was built of sufficient size to treat two tons of ore per day.

In this plant there have been treated 131 charges of ore, and the plant has been run entirely as a self-contained unit—leaching the ore, washing it, purifying and electrolyzing the solutions obtained, and leaching the following lots of ore with the electrolyzed solution from previous charges.

In this plant were treated ores representing the general character of the oxidized ore body at Chuquicamata—some high in copper, others low in copper; some high in impurities, others low in impurities—and enough runs were made to prove the method on both high and low-grade ores, and on ores containing large amounts of salt, as well as smaller amounts of salt, this being the principal impurity in the ore body. The salt deposit, however, is confined to the upper fifty feet of the ore body, and principally to the first twenty-five feet.

In order to make sure that the method should be tested under the most adverse conditions, the same solution was used over and over again for the treatment of the before-mentioned 131 charges of ore, setting aside only enough solution to allow for

the excess acid. A complete analysis of this solution was then made, and showed the following contents:

	Grams per liter
Cu	50.44
Fe	3.71
Mn	0.07
P	0.06
As	nil
Sb	nil
CaO	0.80
MgO	3.32
Al_2O_3	1.61
Na_2O	21.60
K_2O	5.00
SO_3	122.75
Cl	11.52
Free acid (as H_2SO_4)	28.00
Total solids on ignition	189.40
Nitric acid	4.00

The results obtained when using the solution which had previously treated 131 charges of ore were just as good as the results with the solution made from sulphuric acid and water. In other words, the accumulation of impurities has been proven to have absolutely no effect whatever on the results of the leachings obtained. The average extraction obtained in this two-ton plant was 90.99 percent.

Following the experiments in the two-ton plant a leaching tank was built of concrete, lined with mastic asphalt, having a cross-section of 4 x 6 feet and 15 feet deep, holding 15 tons of ore, this allowing the use of the full height of ore column since adopted for the plant now building at Chuquicamata. The question to be decided was whether it was feasible to leach the ore in tanks of this depth. Extensive experimenting gave results confirming those obtained in the smaller tanks.

A wooden filter bottom with cocoa matting on top has been employed in the 2-ton tanks and in the 15-ton tank, although a great number of leachings were made without any filter bottom, simply placing a piece of cocoa matting over the outflow pipe.

All leachings were made without applying any extraneous heat.

The washing of the ore was by the so-called "piston" method, with a final water wash, and the tailings or residues discharged contained an average of about 12 percent moisture and about 0.04 percent water-soluble copper.

Extractions Obtained.

The leaching results obtained up to date are as follows:

	Percent.
The average extraction while treating the ore in lots of 100 kilos each was	90.62
The average of 131 charges treated in the 2-ton plant shows an extraction of	90.99
The average extraction obtained in the 15-ton tank, while treating 25 charges leached up to date, has been	90.96

these results being based on the weight and sampling of the ore as charged into the tanks, and the weight and sampling of the residue discharged from the tanks.

By combining all of these leachings and taking the copper contents based on the weight and sample of the ore treated, as against the copper produced in the electrolytic tanks in the form of cathode copper, together with the copper held in solution as copper sulphate, the extraction was 89.6 percent. The small discrepancy is accounted for by solutions, of which no account has been taken, which have been removed for special tests, as well as spills which will necessarily occur in operating a small-scale plant.

Amount of Chemicals Required.

After having supplied the amount of sulphuric acid required to start the operations, it was found that not only was no further acid required, but that excess acid was produced from the sulphuric acid contained in the ore itself, to such an extent that an actual gain is shown of approximately 9 pounds of acid (H_2SO_4) per ton of ore treated. In other words, it will be necessary to discard an amount of solution equivalent to this gain in acid in order to prevent the acid from accumulating in the process. This gain in acid was made while treating an ore averaging a great deal higher in salt than even the average of the upper layers of the ore body at Chuquicamata will show. As the greatest loss of acid is in forming sodium sulphate, I believe that a still larger gain in acid will be shown when treating the average ore body.

Impurities in Solution.

Of the impurities accumulating in the solution, the principal elements, outside of the chlorine present, are nitric acid, alumina, iron and alkali salts.

After more than a year's work with the same solution, discarding only enough solution to take care of the excess acid, we find the following impurities present:

	Grams per liter
Fe	3.71
Mn	0.07
As	nil
Sb	nil
CaO	0.80
MgO	3.32
Al_2O_3	1.61
Na_2O	21.60
K_2O	5.00
Nitric acid	4.00

This amount of impurities is insignificant so far as their effect upon the leaching and electrolysis is concerned.

The main impurity in our solution is the chlorine obtained from the salt in the upper part of the ore body. It was at first thought desirable to electrolyze direct the solution containing the chlorine, and it was found perfectly feasible to do this in covered electrolytic tanks, maintaining a slight vacuum, so that the chlorine gas was all drawn off through fans. However, it was also proven that only a part of the chlorine was eliminated in that manner, and that an appreciable quantity was deposited with the cathode copper in the form, probably, of cuprous chloride.

Further experimentation proved that it was feasible to eliminate the chlorine from the solution by treatment with shot copper, the reaction taking place resulting in the production of insoluble cuprous chloride. This precipitate settles readily.

Various methods of precipitating cuprous chloride were tried, and finally shot copper, placed in a revolving drum, was adopted as the most satisfactory method. The cuprous chloride forming on metallic copper sticks tight to the copper shot, and it was found necessary to present continuously clean surfaces of copper in order to maintain an effective precipitation. After trying out

several methods it was decided that the best apparatus for this purpose would be revolving drums similar to tube mills, through which the solution would be passed in contact with the shot copper contained in the drums, as in this way the copper, rubbing against itself, continuously presents a clean surface.

Precipitation with cuprous oxide was also tried, and worked very well except that the efficiency of the copper in this form as a precipitating agent was found to be very much lower than that of metallic copper, even allowing for the theoretical difference.

The cuprous chloride produced may be treated in several different ways. It is our intention to filter-press the settled cuprous chloride, mix the filter-press cakes with limestone and coke, and smelt the product thus obtained, producing metallic copper and calcium chloride as a slag. A number of experiments have been conducted with this mixture to establish a reaction, and it has been found that a very liquid slag of calcium chloride is produced containing a very small amount of copper, and that in this manner it is perfectly feasible to smelt the cuprous chloride without any loss by volatilization.

Some small-scale experiments have also been made looking to the electrolytic treatment of the cuprous chloride, and later on it may be possible that this latter method will be adopted, if found more profitable, in preference to the smelting method.

Precipitation of the Copper.

The solution, freed from its chlorine content, is now electrolyzed, using insoluble anodes and ordinary copper cathode starting sheets. After a vast amount of experimenting we have decided to employ an insoluble anode made of magnetite. Various other anodes have been tried with more or less success, but after having investigated all the possibilities we have decided upon the magnetite anodes.

Experiments with these anodes have extended over about a year and a half, and we have found no material amount of chemical wear on the anodes. The magnetite anodes which we have adopted are manufactured by a secret process by the Chemische Fabrik Griesheim Elektron of Frankfort, Germany. The nature of the material naturally gives a brittle anode. How-

ever, as it will not be necessary to handle the anodes after they are installed in the tanks, this is not a very decided drawback.

At first a number of difficulties were encountered in our efforts to secure an even current distribution and proper suspension of the anodes, but all of these obstacles have been overcome, and we believe that a very serviceable anode has been developed.

The anodes themselves are hollow castings with a wall thickness of approximately 0.25 inch (0.63 cm.), and have a thin electroplated copper deposit on the inside.

As I am not myself familiar with the methods employed in the manufacture of these anodes, I am unable to give any further information on this point. I can only state that, after months of continuous operation, we have found the anodes entirely satisfactory for our purpose.

The copper cathodes produced from the electrolysis are of the usual quality of cathode copper; in fact, a little better, as in our particular case no arsenic or antimony—usually the most deleterious impurities in cathode copper—is present in the solution.

The solution will enter the head tank of the electrolytic system containing approximately 5 percent copper and 2½ to 3 percent free acid, and will leave the last tank of the cascade containing about 1.5 percent copper and 8 to 9 percent free acid. Within these limits it is always possible to produce a good, hard cathode, equal to or better than the usual standard.

The electrolytic tanks used during our experiments are made of concrete lined with mastic asphalt.

DESIGN OF PLANT NOW BUILDING AT CHUQUICAMATA.

On account of the very large ore body already developed at Chuquicamata, the first unit of the plant now building has been designed to treat about 10,000 tons of ore per day. The electrolytic refinery will have a capacity of about 335,000 pounds (152,000 kg.) of copper per day.

The ore will be mined by steam shovels, practically no stripping being necessary. The ore will be transported to the mill, distant about 2½ miles (4 km.) from the mine, in standard American gauge railroad cars of 60 tons' capacity each.

Arriving at the plant the ore will first pass through gyratory

crushers, thence through 48-inch Symons disc crushers, and finally through Garfield rolls, until a product is obtained of about 0.25 inch (0.63 cm.) mesh. The ore will be carried on conveying belts from the crushing plant, after sampling, to the leaching vats. Each of the leaching vats has the following dimensions: 110 feet (33 m.) wide, 160 feet (48 m.) long and 16 feet (4.8 m.) high. The leaching vats, six in number, will be placed end to end.

The belt delivering the ore from the crushing plant will be discharged into the leaching vats with the aid of an electric traveling bridge, spanning and traveling the entire length of the leaching tanks. The leached and washed residue will be removed from the leaching tanks by a 15-ton grab bucket traveling on an unloading bridge, and, after sampling, will be delivered on to a conveying belt for disposal to the tailings dump.

The tanks are being built of heavily reinforced concrete, and will be lined with mastic asphalt 1½ inches thick. This tank lining has been developed by the Vulcanite Paving Company of Philadelphia, and consists of a specially refined Trinidad asphalt mixture, to which is added crushed quartz or granite.

In our experimental plant, where this lining has been in use for considerably more than a year, both in the leaching and electrolytic tanks, absolutely no difficulty—not even a single leak—has developed. We have tested the material at a temperature of 50° C. without finding any signs of softening, and, as this is far beyond the range at which we intend to operate, tests at higher temperatures have not been made, although the temperature limit, so far as softening is concerned, will probably lie somewhere between 50° and 70° C.

Tests have also been made to try the strength of this material from a physical standpoint, and in one case a 250-pound cathode was elevated about 5 feet above the bottom of the tank and then dropped in such a way that one of the sharp corners of the cathode hit the bottom of the mastic asphalt lined tank. In this case a piece of the lining about ⅛ inch (0.3 cm.) thick and 2 inches (5 cm.) in diameter was broken away, and as far as we could see the tank lining was just as good as ever.

The material has been tested in strong and weak acid solutions, and found to be absolutely unattacked.

From the bottom of the leaching tanks the solution will be removed through eight 6-inch openings equally distributed over the tanks.

A filter bottom, consisting of two layers of 2-inch planks with a layer of cocoa matting between, will be employed. This filter bottom will be raised 4 inches above the bottom of the tank.

For the main solution circuits, 9-inch (22 cm.) and 16-inch (40 cm.) lead-lined iron pipe will be used. Open-boot horizontal centrifugal pumps, made of type-metal, will be used for pumping the solutions. The pumps will have a capacity of 550 cubic feet (15.5 cu. m.) per minute, elevating to a height of 60 feet (18 m.).

In the leaching plant the cycle of operation will require approximately six days, of which one day will be occupied in filling the tank, two days in leaching, two days in washing and draining, and one day in discharging.

The solutions will be conducted to the leaching tanks by gravity from nine solution storage tanks placed above the leaching tanks. The dimensions of these solution storage tanks are as follows:

Two tanks 12 x 130 x 150 feet (3.6 x 39 x 45 m.).
Seven tanks 12 x 70 x 150 feet (3.6 x 21 x 45 m.).

From the strong solution tank the solution will flow by gravity through the dechlorinating plant, consisting of twenty-one 30 feet (9. m.) long by 4 feet (1.2 m.) inside diameter revolving steel drums lined with earthenware. These drums will be half full of shot copper. From these drums the solution, containing the cuprous chloride in suspension, will flow to seven Dorr thickeners made of concrete and lined with mastic asphalt. The clear solution overflowing will travel by gravity to the electrolytic refinery, while the thickened cuprous chloride, together with approximately 1 percent of the original solution, will go to filter presses.

The electrolytic refinery will consist of 510 electrolytic tanks of the following dimensions: 19 feet (5.7 m.) long, 3 feet 6 inches (1.05 m.) wide, 4 feet 10 inches (1.5 m.) deep. They will be made of concrete, lined with mastic asphalt, and will

be set through the floor, having inspection aisles underneath and a concrete working platform between the rows of tanks. The tank-house will be of concrete and steel construction.

Of the 510 tanks, 30 will be used for making cathode starting sheets, and the balance, 480 tanks, will be used for electrolytic deposition of the copper from solutions. The tanks will be arranged in five electrical circuits, with 96 tanks to a circuit, and will be divided into 30 solution circuits, the solution in each circuit flowing through 16 tanks placed in cascade.

The anodes, made of magnetite, will be 5 inches (13 cm.) wide, 2 inches (5 cm.) thick and 4 feet (120 cm.) long, with five to a bar. The cathodes will be 3 feet (90 cm.) wide by 4 feet (120 cm.) deep.

The spent electrolyte, containing about 1.5 percent copper, will be pumped back to the storage tanks, to be used for leaching subsequent charges of ore.

The cuprous chloride from the dechlorinating plant will be smelted and cast into shot copper for use in the dechlorinating drums.

The power plant will consist of a primary power station at the coast, using oil-fired Babcock & Wilcox boilers driving four steam turbines connected to four 10,000 kw. alternating current generators. The current will be transmitted 85 miles at 100,000 volts to a sub-station located at the mill-site. The sub-station for the electrolytic refinery will consist of seven motor-generator sets, each of 2,500 kw. capacity.

CONCLUSION.

It will be readily understood that a vast amount of experimental work has been conducted in order to arrive at a satisfactory solution of the problems before us in connection with the ores from Chuquicamata, and a great many negative results have been obtained as well as positive results. From fifteen to twenty young engineers have been continuously employed for more than a year on this experimental work, the experimentation going on steadily in three 8-hour shifts.

It has been our endeavor in conducting the experiments to operate each part of the apparatus on what we might term a cross-section scale of the plant to be erected at Chuquicamata.

We have thus used a leaching tank with the full depth of ore column, the important point in leaching, and we have used the same material for filter bottoms as will be used in the large plant. We have had full-size solution valves installed. In connection with the dechlorinating plant we built a full cross-section drum. In the electrolytic tanks we have been operating with full-size cathodes and anodes. In short, the idea has been to approach in our experiments, as far as possible, operating conditions similar to those which we will have in the large plant.

I wish to take this opportunity to state that great credit for the results obtained should be given to the loyal and enthusiastic staff employed, and I will particularly mention in this connection Mr. C. A. Rose, in charge of the experimental work at the plant, and his able assistant, Mr. Leonard M. Green, who, under Mr. Rose, has had charge of the leaching part of the experiments and who has developed the details of the leaching and washing system now adopted, and Mr. M. R. Thompson, who has had charge of the electrolytic part of the experiments.

DISCUSSION.

JOSEPH W. RICHARDS: I would like to ask Mr. Smith what difficulty has been found with the poor conductivity of these anodes—what difference of voltage was there between the top of the anode and the bottom, what proportion of the current seems to go by preference to the top of the anode from the bottom?

E. A. C. SMITH: The main trouble seems to be that there was an uneven deposit of copper on the inside of the anodes, which seems to be more of a plating deposited at the top than at the bottom. We took it up with our German friends, and got them to plate the anode solidly all the way down, and that cured the difficulty. It was not the resistance of the materials so much as the uneven distribution of the electroplated copper on the inside.

LAWRENCE ADDICKS: I understand that the cathodes produced are free from chlorides, on account of the purification system,

whereby chlorides are removed from the electrolyte, or the cuprous chloride in the cathodes gives no trouble in the free copper alloys when melting?

E. A. C. SMITH: The presence of chloride in the cathodes, as made today, amounts to about 0.001 percent.

LAWRENCE ADDICKS: Practically free from chlorine?

E. A. C. SMITH: Yes.

JOSEPH W. RICHARDS: I ask Mr. Smith whether he has analyzed any of the anode material, and whether it is substantially Fe_3O_4? Of course, anyone who got hold of a piece of it could analyze it.

E. A. C. SMITH: It carries a very small amount of silica.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

THE HYDRO-ELECTROLYTIC TREATMENT OF COPPER ORES

By Robert Rhea Goodrich.

It is the intention of this paper to give a brief summary of the practised and suggested hydrometallurgical processes for the extraction of copper from its ores. The review of the literature as given contains the salient points of what has been done in the history of the subject.

The problems of economically treating low-grade copper ores have turned the attention of metallurgists toward such hydrometallurgical problems as are encountered with low-grade siliceous, oxidized and sulphide ores, and concentrates, especially where water-power is cheap and fuel is expensive. The treatment of tailings from concentrates is another promising field for leaching methods, there being no other known possible method for economically extracting their copper contents. The same is also true of complex refractory ores which are not amenable to smelting for the recovery of their several metals. And, lastly, there are metallurgists who entertain hopes of discovering a leaching method which will radically change all methods of copper extraction to something quicker and cheaper than the present smelting methods.

Classification of Hydrometallurgical Processes.

I. Purely Chemical Methods:

1. ***Alkali processes.***
2. ***Sulphite*** "
3. ***Sulphate*** "
4. ***Chloride*** "

Copper is dissolved and precipitated by chemical reagents.

II. Electrolytic Methods:

1. ***Sulphate processes.***
2. ***Chloride*** "

Copper is dissolved chemically and is precipitated electrolytically. The deposition is usually accompanied by regeneration of the solvent.

All acids react more or less with the constituents of the ore, causing:

a. Consumption of acid.

b. The bringing in of elements detrimental to the process.

Iron, arsenic, antimony and bismuth, while detrimental, are not necessarily fatal to an acid process. If lime, magnesia, zinc or manganese occur in large quantities in the ore, acid processes are not applicable—the limit can only be determined by experiment. While calcium carbonate is detrimental, calcium sulphate is not. Alumina is undesirable, but not necessarily very injurious.

Many oxidized ores are improved by roasting.

All sulphide ores require roasting for most of the leaching processes, the exception being chalcocite ores, which may be leached direct. (Greenawalt, "Hydrometallurgy of Copper," 1912 Ed., Chap. IX.)

I. Purely Chemical Methods:

1. Alkali Processes.

The alkali processes have not met with much encouragement in the hydrometallurgical extraction of copper from its ores, due largely to the low and slow solubility of copper minerals in solutions of the alkalies. Ammonia and ammonium compounds are the only alkaline solvents tried for the leaching of copper oxide ores on a commercial scale. (Greenawalt, p. 172.)

The Mosher-Ludlow Ammonia-cyanide Process.

This process is applicable to ores containing oxide and carbonate of copper. At the ordinary temperature, ammonia (NH_3) forms a stable compound [$Cu(NH_3)_2$] which readily dissolves in water containing slight excess of ammonia. At the boiling point of the solution the compound is broken up, hydrated copper oxide being precipitated. The distilled ammonia may be condensed and used for further treatment of the ore. When the ore contains gold and silver as well as copper, a weak solution of potassium cyanide is used to extract the precious metals

subsequently to the copper. The gold and silver are precipitated by zinc. (Electrochemical and Metallurgical Industry, Mar., 1908, p. 128; Greenawalt, p. 172.)

2. *Sulphite Processes.*

The *Neill Process* is applicable to ores containing oxide and carbonate of copper. When cupric oxide is treated with water through which sulphur dioxide is passed, the following reaction takes place: $3CuO + 3SO_2 = 3CuSO_3$. The cupric sulphite formed is insoluble in water, but is readily soluble in water containing an excess of sulphur dioxide. This constitutes the leaching step. Then the clear liquid is drawn from the ore and heated to drive off the excess sulphur dioxide, when a bright red, heavy precipitate [$Cu_2SO_3.CuSO_3$] is thrown down. Next, the liquid is run over iron to precipitate any copper that may remain in solution as sulphate. The liquid which contains no copper finally goes to waste. The experimental plant of the Montana Ore Purchasing Co., at Butte, was put up by Neill. Washing was difficult on account of ferric oxide which formed in the leaching charge. The results were: Ore, 3.15 percent Cu; tailings, 0.31 percent Cu; extraction 90 percent. (Greenawalt, p. 178.)

The *Van Arsdale Process* consists in precipitating the copper from cupric sulphate solution by adding sulphur dioxide ($3CuSO_4 + 3SO_2 + 4H_2O = [Cu_2SO_3.CuSO_3] + 4H_2SO_4$), and heating with or without pressure ($Cu_2SO_3.CuSO_3 + 4H_2SO_4 = Cu + 2CuSO_4 + 2H_2SO_4 + 2SO_2 + 2H_2O$), thereby simultaneously regenerating acid solution for leaching the ore. The regenerated sulphuric acid is double the amount required to dissolve the amount of copper precipitated. Only a part of the copper is precipitated. The process being cyclic, there is no particular harm in returning to the ore a solution containing a considerable amount of unprecipitated copper sulphate. (E. and M. J., June, 1908; U. S. Patent, Mar. 31, 1903, No. 723,949; Greenawalt, p. 179.)

3. *Sulphate Processes.*

Oxidized ores containing copper as oxide or carbonate may be treated directly with dilute sulphuric acid solutions. Sulphide ores, with the possible exception of certain chalcocite ores, should

be roasted prior to leaching. The copper may be dissolved as sulphate either by (1) sulphuric acid or (2) metal sulphates. Reactions during leaching with sulphuric acid are: $CuO + H_2SO_4 = CuSO_4 + H_2O$, and during precipitation: $CuSO_4 + Fe = Cu + FeSO_4$. Theoretically, 1.68 lb. 66° B. sulphuric acid and 0.88 lb. iron are required to produce 1 lb. of copper.

Copper has been dissolved from its ores by ferric sulphate solutions containing free sulphuric acid: $xH_2SO_4 + Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S + xH_2SO_4$. Cuprous sulphide is slowly acted upon by solution of ferric sulphate. Most of the improvements of this simple process are based on the regeneration of the solvent. (Greenawalt, p. 180.)

Sulphuric Acid Leaching of Oxidized Copper Ores at Clifton, Arizona.

The Arizona Copper Company has been leaching oxidized surface ores at Clifton on a large scale since 1893.

The sulphuric acid is manufactured from roaster gases. The Joy Mine, Morenci, furnishes the pyrite ore, containing 1.5 per-cent copper, which is crushed to 2-inch. The fines are roasted in a Herreshoff five-deck furnace. The coarse material goes to lump burners. The cinder from the roasting furnaces is smelted in blast furnaces. The resulting acid (chamber acid) is 52° B.

The ore which contains 2.5 percent of copper is conveyed from the mines at Metcalf to the "Oxide Mill" at Clifton. The copper exists chiefly as malachite, together with some sulphides. By wet concentration, 25 percent of the copper is extracted as concentrates, carrying 7 to 10 percent of copper, which are smelted. Slimes carrying 2.4 percent of copper go to the slime pond for settling; they contain too much soluble alumina to leach. The tailings, size 1 inch to sand—75 percent of them larger than ⅛ inch—go to the leaching vats. Circular wooden vats, with perforated false bottom for filter, are used for leaching. The solution is circulated by centrifugal pumps, one being supplied to each tank. Successive solutions are applied. The first solution to fresh ore (concentrator tailings) is one high in copper and low in acid. This solution, leaving the vat with practically no free acid, passes on to the precipitation tanks. There is then applied to the ore a solution containing more free acid and less

copper, followed by a fresh acid solution and lastly a water wash. The copper contents of the liquors is precipitated on scrap iron. There being no free sulphuric acid, the consumption of iron is a minimum. Liquors free from copper are run to waste in earthen reservoirs and sink in the ground, thereby preventing contamination of the streams. There are consumed 2.6 lb. of 52° B. acid (1.82 lb. 66° B. Com.) per pound of copper extracted. No general rule can be given for strength of acid. The more soluble the gangue, the weaker should be the acid. The ore carries a trace of gold, which apparently is lost. (Greenawalt, p. 183.)

Leaching Plant at the Snowstorm Mine.

The vein at Larson, Idaho, is a replacement in quartzite. Only the oxidized ore of the upper workings (consisting of cuprite, malachite and chrysocolla) is treated. The copper content is 3 percent, with small gold and silver values. The process is: Crush the ore and treat in agitators with bleaching powder and sulphuric acid, thus converting the copper, gold and silver into chlorides. Separate the liquor, and precipitate the copper and gold on scrap iron. Treat the residue with hyposulphite of soda to dissolve the silver chloride, which subsequently precipitate by sodium sulphide. The saving is 90 percent of assay value of the ore. (Greenawalt, p. 187.)

Copper Leaching Plant at the Gumeshevsky Mine, Russia.

The mine was shut down in 1871. The mine owners contracted with an acid manufacturer to manufacture acid on the property from pyrite carrying 3.5 to 8 percent of copper; to sell 53° B. acid to them at $4.32 per ton; to extract the copper from the burned pyrite, leaving less than 0.3 percent of copper in the tailings; to pay the owners $145 to $175 per ton of copper produced. The method used to extract the copper from the burned pyrite was: Roast burned pyrite with addition of sulphuric acid in a muffle furnace at 450° C. to 550° C., bringing copper into soluble condition; leach with water; leach with barren solution after precipitating on cast iron plates; leach with dilute sulphuric acid; precipitate copper at boiling temperature on cast iron plates. Consumption of acid, 2 lb. (66° B. Com.), and of cast iron, 1 to 2 lb. per pound of copper produced.

The mine owners worked the extensive dump left from the earlier working of the mine, when it was worked for oxidized ore only. The process was: Crush dump material by rock breaker and Chilean mills; leach with dilute sulphuric acid; precipitate copper by cast iron, granulated or in plates. The oxidized dump material treated contained 0.75 percent copper; of this 0.43 percent was recovered, the balance going into the tailings. Extraction, 57 percent. Insoluble copper existed as silicate and native copper. Consumption of acid, 7.4 lb., and of iron, 1.9 lb. for 1 pound of copper produced. Thus only 23 percent of acid consumed was usefully employed in dissolving copper; the balance acted on worthless gangue. All tanks, both for leaching and for precipitating, were rectangular and made of concrete. The agitator moved longitudinally in the leaching tank. (Greenawalt, p. 187; Inst. of Min. and Met. Bull., No. 65; Trans. I. M. M., XIX, p. 212; Min. Ind., 1910, p. 210.)

The Laist Process.

The process is based on the use of sulphuric acid as the solvent and hydrogen sulphide as the precipitant. The steps in the process are as follows:

1. Dissolving copper with dilute sulphuric acid: $CuO + H_2SO_4 = CuSO_4 + H_2O$.

2. Precipitating copper by hydrogen sulphide and regenerating sulphuric acid: $CuSO_4 + H_2S = H_2SO_4 + CuS$.

3. (a) Manufacturing hydrogen sulphide by reducing calcium sulphate (gypsum) with coal, which takes place at 1800° F. (982° C.): $CaSO_4 + 4C = CaS + 4CO$.

(b) Decomposing calcium sulphide by carbon dioxide and water to hydrogen sulphide and calcium carbonate: $CaS + H_2O + CO_2 = H_2S + CaCO_3$.

4. Converting copper sulphide precipitate to metallic copper by roasting and reducing in furnaces. In practice there was used for reaction 3 (a) about 2⅔ lb. gypsum and 1¼ lb. of coal, which is but slightly above the theoretical amount. (Greenawalt, p. 204.)

Roasting and Leaching Tailings at Anaconda, Montana.

During the summer of 1912 experiments were made on regular concentrator tailings by roasting and leaching. The results were so satisfactory that it was decided to continue the work on a larger scale. In February, 1913, construction was begun on an 80-ton roasting and leaching plant. It was decided to precipitate copper by scrap iron and to experiment with precipitation by electrolysis and by hydrogen sulphide.

The roasting experiment was conducted in a regular No. 64 improved McDougal furnace. Two fire boxes were placed so that the flame could enter the third or the fourth floor (from the top). The third floor was selected as the better. The best results were obtained by oxy-chloride roasting. The firing was regulated by a pyrometer inserted on the fourth floor. The temperature was held at 1000° F. (538° C.). On the upper three hearths the ore was partly roasted. One percent by weight of sodium chloride was added on the fourth floor.

The leaching was by percolation: No. 1 solution contained 3.5 percent of H_2SO_4 and 10 percent of NaCl; No. 2 solution contained 6 percent of H_2SO_4 and 10 percent of NaCl. Then followed water washes. The precipitation was done by hydrogen sulphide. No. 1 solution was the only one precipitated. No. 2 solution became No. 1 solution on the next vat. The acid strength was brought up in the precipitating vat. It was not necessary to add salt (NaCl), as the solution picked it up from the roasted ore.

Summary of two months' operation:

In calcines to leaching plant: 10.4 lb. copper per ton, 0.46 oz. silver per ton.

Percentage of recoverable copper, 85.4 percent; percentage of recoverable silver, 91.1 percent.

Conclusions:

It is not advisable to leach high-grade 3 percent copper material, which may be concentrated.

Material should be crushed to 15-mesh preparatory to roasting and leaching.

Copper set free by crushing should be taken out as high-grade concentrate and smelted.

Sulphuric acid can be cheaply made at a smelting plant.

It is estimated that copper can be produced for 6.5 cents per pound. This is possible because tailings are already mined, crushed and sized; cheap acid may be made from roaster gases; operations are on a large scale. (M. and E. W., Vol. 39, No. 13, p. 545, Sept. 27, 1913; No. 14, p. 599, Oct. 4, 1913; Frederick Laist.)

Experiments with Ferric Sulphate at Cananea.

The dissolving of cuprous sulphide from the ores, by means of ferric sulphate solution, is in accordance with the reaction: $Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$. Thus, for 1 lb. of copper going into solution, 6.3 lb. of anhydrous ferric sulphate is reduced. Copper oxide is dissolved by ferric sulphate solutions, as expressed by: $3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3$. Thus in dissolving copper oxide, 2.1 lb. anhydrous ferric sulphate is consumed for 1 lb. copper going into solution.

At Cananea the consumption was found to be 4.37 lb. ferric sulphate per pound of copper extracted. The content of solution in ferric sulphate was of small import, provided basic iron salts were absent from it. The solution worked with as small an amount as 1 percent. The extraction with a 2 percent solution was nearly as complete as with a 7 percent solution. From leaching, the liquor went to the precipitation tank, in which iron was used for precipitating the copper according to: $CuSO_4 + Fe = FeSO_4 + Cu$. While the theoretical consumption of iron is 0.88 lb. for 1 lb. copper precipitated, the actual consumption was 1.5 times this amount. The solution was regenerated for further leaching by blowing hot air through the heated solution, as shown by: $10FeSO_4 + 5O = 3Fe_2(SO_4)_3 + 2Fe_2O_3.SO_3$. Thus with a neutral solution, 40 percent of the iron content is precipitated as a basic salt ($2Fe_2O_3.SO_3$). To prevent the formation of basic salt during the regeneration in the oxidizer, sulphuric acid must be supplied in an amount as indicated by: $2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$. Since acid must be replenished, the process becomes virtually one of leaching with acid. In treating mill tailings, 65 percent of the copper was

extracted in 3 hours (liquor boiled). In treating a 10-ton lot of Cobre Grande ore containing 3 percent of copper, extraction was 96 percent. The cost per pound of copper was 6.4 cents. There was much trouble with the oxidizer in the regeneration of the spent liquor. (Greenawalt, p. 194; Mines and Methods, Sept., 1910, W. L. Austin).

Thomas's Experiments with Ferric Sulphate on Sulphide Ore.

The results were: Double sulphides of copper, which occur in nature, require for complete transformation by ferric sulphate, long treatment with fine crushing. The commercial application does not pay. Free copper sulphides and oxides react easily with ferric sulphate in aqueous solution. Double sulphides of copper (such as chalcopyrite) must be roasted. Roast at low temperature (sulphatizing), 450° C. to 480° C., to produce the maximum amount of copper sulphate. The copper may then be leached with but small amount of ferric sulphate. (Greenawalt, p. 201; Metallurgie, Jan. 15, Feb. 8, 22, 1904.)

Methods of Extracting Copper at Rio Tinto, Spain.

The ore is massive pyrite containing 3 percent of copper, mostly as cuprous sulphide. The method in use at the present time is weathering, or aid-oxidation. The reactions are: $FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$. Ferrous sulphate readily oxidizes, forming ferric sulphate: $2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$. Half the copper goes in solution in a few months, reducing an equivalent of ferric sulphate: $Fe_2(SO_4)_3 + Cu_2S = CuSO_4 + 2FeSO_4 + CuS$. The following reaction is slow, taking two years to extract 80 percent of the remaining half: $Fe_2(SO_4)_3 + CuS + 3O + H_2O = CuSO_4 + 2FeSO_4 + H_2SO_4$. The process is: Ore is piled in heaps containing 100,000 tons, with flues of rough stone at the base connecting with chimneys. The oxidation goes on rapidly. The temperature rises, but is not allowed to go above 170° F. (77° C.) at chimneys, otherwise the heap might catch fire. The regulating of the temperature is accomplished by closing the tops of chimneys. Water is run on top of the heap, leaching the copper. The outflowing copper solution, before going to the precipitation tanks, is sent to the filter bed of fresh ore, thus reducing any contained ferric sulphate and insuring minimum consumption of iron: $7Fe_2(SO_4)_3$

$+ FeS_2 + 8H_2O = 15FeSO_4 + 8H_2SO_4$. After a year or two the copper contents is reduced to 0.3 percent, corresponding to 90 percent extraction. The ore is disposed of as "washed sulphur ore" (containing 49.5 percent S), which is used for the manufacture of sulphuric acid; 99.5 percent of the copper in the liquor is precipitated with a consumption of 1.4 lb. pig iron (92 percent Fe) per pound of copper recovered. (Greenawalt, p. 205; T. A. I. M. E., Vol. XXXV, 1905, C. H. Jones.)

Leaching Shannon Copper Ores.

Experiments were made by Francis S. Schimerka to find a practical leaching system for treating low-grade ore and tailings. The basic character of the ore makes sulphuric acid leaching impossible on account of the high acid consumption. Treatment with roasting gases gave successful results. The ore contained 1.9 percent of copper, 0.55 percent of sulphur and a minute trace of gold and silver. The direct leaching with sulphuric acid gave an extraction of 81 percent, with acid consumption of 8.8 lb. per pound of copper extracted. The process employed was: The ore was subjected in heaps to roasting gases. At the base of the heap were constructed flues connecting with chimney for firing. At the bottom was placed a layer of 100 tons of pyrite containing 50 percent of sulphur; then 1,000 tons of oxide ore, crushed to 2 inch, was placed on top, and finally covered with a layer of fines a foot thick. The heap was sprinkled with waste solution from the scrap-iron precipitation tanks, producing ferric sulphate according to: $2FeSO_4 + SO_2 + O_2 = Fe_2(SO_4)_3$. The roasted ore was leached with water in tanks with filter bottoms. The ferric sulphate formed by roasting dissolves copper which may not be water soluble. The outflowing copper solution, still containing some ferric sulphate, was run over tailings to reduce the last of the ferric sulphate before going to scrap-iron for precipitation of the copper. Extraction, 72 to 82 percent. The advantages of this process are: (1) Coarse crushing; (2) cheap installation; (3) *no* sulphuric acid used; (4) commercial use of ferric sulphate solution, produced in excess of requirements.

Laboratory experiments by Francis S. Schimerka, on the treatment of ore and tailings, were conducted by roasting these materials in a muffle furnace and treating, as follows:

1. Ore containing 2.37 percent Cu, 3.02 percent S, was roasted at 535° C. Leached with 5 percent H_2SO_4 solution. Extraction, 86.4 percent. Consumption of acid, 3.19 lb. per pound of copper extracted—permissible in commercial practice.

2. Ore containing 2.01 percent Cu, 2.58 percent S. Ferrous sulphate was added in such amount that iron (Fe) was 2.8 percent the weight of ore. Leached with 10 percent H_2SO_4 solution. Extraction, 82.5 percent. Consumption of acid, 1.2 lb. for 1 pound copper extracted.

3. Tailings, product of concentration of sulphide ores (basic in character), containing 0.83 percent Cu, 0.88 percent S, were roasted with addition of pyrite in largest amount permissible for profitable working. When using sulphuric acid for the leaching the lowest consumption was 7.41 lb. acid per pound of copper extracted. Extraction 60 percent.

4. Tailings, treated like sulphide ores. Ferrous sulphate added in such amount that iron (Fe) was 1.4 percent weight of ore. Roasted at 480° C. Ferric sulphate in roasted ore was 1.01 percent. Water was added in amount equal to the weight of ore. Digested twelve hours with cold solution. Extraction 71.7 percent. (E. and M. J., Vol. 96, No. 24, Dec. 13, 1913, p. 1107.)

4. Chloride Processes.

The chloride processes have been widely applied. Hydrochloric acid presents certain advantages over sulphuric acid in technical application. Hydrochloric acid is less apt to form basic salts, and therefore yields solutions that contain but little free acid and which constantly require less iron for the precipitation of copper. Hydrochloric acid is usually more expensive than sulphuric acid. Ordinarily only oxidized ores are suitable to treatment by a chloride process. The copper may be dissolved by hydrochloric acid, or by a metal chloride. The reaction which occurs is: $CuO + 2HCl = CuCl_2 + H_2O$. (1.15 lb. HCl per pound Cu.) The precipitation of the copper is expressed by: $CuCl_2 + Fe = FeCl_2 + Cu$. (0.88 lb. Fe per pound Cu.) Theoretically, the same amount of iron is required for the precipitation as for precipitation of copper from sulphate solutions. Practically, sulphate solutions consume more iron than chloride solutions. (Greenawalt, p. 216.)

In Stadtberg, Westphalia, hydrochloric acid was formerly used to extract copper from ores containing 1 to 2 percent of copper. The process replaced a sulphuric acid process previously employed, but was abandoned when carbonates of the ore changed to sulphides in depth. The ore was leached in rectangular wooden tanks containing 90 tons. The fresh ore was treated with partially saturated solution until saturation took place. Ore nearly copper-free was treated with fresh 12.5° B. acid, and lastly with water wash. Acid consumption, slightly above the theoretical. (Schnabel, "Handbook of Metallurgy," Vol. I, p. 200; Greenawalt, p. 217.)

Ferric chloride, like ferric sulphate, dissolves copper from ores containing the metal as oxide, carbonate and sulphide. (Cu_2S is the only sulphide easily soluble.) The reactions are: $Cu_2S + 4FeCl_3 = 2CuCl_2 + 4FeCl_2 + S$, and $3CuO + 2FeCl_3 = 3CuCl_2 + Fe_2O_3$. The copper may be precipitated by iron: $CuCl_2 + Fe = FeCl_2 + Cu$. Regeneration of the ferric solution may be accomplished by means of air, causing one-third of the iron to precipitate: $6FeCl_2 + 3O = 4FeCl_3 + Fe_2O_3$. It may be regenerated by chlorine, produced chemically or electrolytically: $FeCl_2 + Cl = FeCl_3$. (Greenawalt, p. 218.)

Doetsch Process.

This process was formerly applied to raw and to roasted ores at Rio Tinto, Spain.

1. Raw ores. The ore contained 2.7 percent of copper. The pyrite was unaffected by leaching solutions. The process is: Crush to ½ in. Mix with 0.5 percent by weight of sodium chloride and 0.5 percent of ferrous sulphate. Build in large heaps. Run on solution of ferric chloride. Precipitate copper on pig iron. Regenerate solution in scrubbing towers by chlorine generated by roasting, according to: $2FeSO_4 + 4NaCl + 3O = Fe_2O_3 + 2Na_2SO_4 + 4Cl$. Extraction, 50 percent in 4 months, 80 percent in 2 years. Consumption of pig iron, 1.3 lb. per pound of copper produced. Cumenge estimates the cost as 3.3 cents per pound of copper.

2. Roasted ores. The ore of nut size is made into heaps of 800 tons, with 14 tons salt. Rough flues 20 inches square, used for firing, are constructed at the bottom and connected with

chimneys. The reaction is shown by: $2FeSO_4 + 4NaCl + 3O = Fe_2O_3 + 2Na_2SO_4 + 4Cl$. The liberated chlorine produces ferric chloride and cupric chloride. Some of the roasted ore has been mixed at times with the unroasted ore for the extraction of the copper by the ferric chloride solution. (Greenawalt, p. 219; Annales des Mines, Vol. XCVI; Notes Sur le Rio Tinto, M. E. Cumenge.)

The Froelich Process.

The ore is subjected, in the absence of air, to temperature between 150° C. and 800° C. Chlorine gas is introduced. After chlorinating, in order to regain the chlorine combined with the iron, heat to above 300° C., introducing a certain amount of air, when the ferric chloride is evaporated, and in the presence of air is decomposed into ferric oxide and chlorine. The cupric chloride is not changed by this treatment. Leach with water. Precipitate copper by iron. Oxidize ferrous chloride to ferric chloride in rotating drum by a blast of air. Drive off water of crystallization of ferric chloride. Heat to about 300° C. with a certain amount of air, thus regenerating chlorine for the process. (Greenawalt, p. 223; U. S. Patent No. 846,657, Mar. 12, 1907.)

Ferrous Chloride Process.

Some years ago Hunt and Douglas based a process on the action of ferrous chloride on copper oxide and copper carbonate. Hunt says that chrysocolla ($CuSiO_3 + 2H_2O$) is likewise completely decomposed by a hot solution of ferrous chloride containing sodium chloride. The reaction given is: $3CuO + 2FeCl_2 = CuCl_2 + 2CuCl + Fe_2O_3$. The precipitation by metallic iron is said to be according to: $CuCl_2 + 2CuCl + 2Fe = 2FeCl_2 + 3Cu$. Cuprous chloride, which is insoluble in water, is soluble in solutions containing an excess of metal chlorides. Silver in ore is converted to silver chloride by cupric chloride, and is dissolved in solutions containing an excess of metallic chlorides. Theoretically, 0.59 lb. iron precipitates 1 lb. copper. An objection is that basic salts of iron clog the filter. Heat is not necessary, but it hastens the reaction. The silver will be precipitated with the copper. If it is desired to precipitate the silver separately, reduce all cupric chloride to the cuprous state by means

of sulphur dioxide, then precipitate the silver on copper, and subsequently copper on iron.

The process, as formerly applied at Ore Knob, Ashe Co., N. C., is: Crush the ore to 40 mesh and roast to sulphate and oxide. Leach with hot solution of ferrous sulphate and sodium chloride (22° B.). Precipitate copper on iron, regenerating solvent: 0.7 lb. iron precipitates 1 lb. of copper. Cost of the copper, 8 cents per pound. (Greenawalt, pp. 225-6; T. A. I. M. E., Vol. X, p. 12; T. A. I. M. E., Vol. II, p. 394, E. E. Olcott.)

Hunt and Douglas Process.

This process is based on the following combination reaction: $2CuSO_4 + 2NaCl + SO_2 + 2H_2O = 2CuCl + Na_2SO_4 + 2H_2SO_4$. The process is: Roast, if the ore is a sulphide, and extract the copper from the oxidized ore with dilute sulphuric acid regenerated in the process. Convert the cupric sulphate into cupric chloride by addition of a soluble chloride. Convert soluble cupric chloride into insoluble cuprous chloride by sulphur dioxide, with simultaneous regeneration of sulphuric acid. Convert the precipitated cuprous chloride into cuprous oxide, or metallic copper, by addition of milk of lime or replacement with iron. If the roasted ore contains silver, the sulphate of copper, which in well-roasted ore should be one-third of the content, is first leached out with water, care being taken to add just sufficient soluble chloride to render insoluble any silver present. From the clear solution thus obtained, after adding the requisite amount of sodium chloride to chloridize the copper, precipitate the copper by sulphur dioxide. The resulting liquor, freed from sulphur dioxide, is used to dissolve the oxide of copper in the ore. From the residues the silver may be extracted by brine, after which the gold may be recovered by chlorination. Chloride of silver is soluble to some extent in a solution of cupric chloride, and is then in part carried down with the cuprous chloride. (Greenawalt, p. 228; T. A. I. M. E., Vol. X and XVI.)

Hunt and Douglas Process at Argentine, Kansas.

At the Kansas City Smelting and Refining Company's works the material treated was a lead-copper matte. In applying the process, using sodium chloride as chloridizer, sodium sulphate

accumulated in the solution, which crystallized out, causing trouble. This trouble was corrected by using three parts of calcium chloride and one part of sodium chloride as chloridizers. Calcium sulphate formed, and, being insoluble, was precipitated. The necessary calcium chloride was produced in the process, in the conversion of cuprous chloride to cuprous oxide by milk of lime. The residue from the leaching went to the lead smelting department. (Greenawalt, p. 231; Mineral Industry, Vol. XVII, 1908, p. 296.)

Modification of the Hunt and Douglas Process.

To simplify the operation, Hofmann worked out and successfully introduced the following modifications: Roast ore or matte as usual. Treat roasted ore or matte in agitating tanks with dilute sulphuric acid produced in the process: $H_2SO_4 + CuO = CuSO_4 + H_2O$. Chloridize with hydrochloric acid produced in the process, regenerating sulphuric acid: $CuSO_4 + 2HCl = H_2SO_4 + CuCl_2$. Convert the soluble cupric chloride into insoluble cuprous chloride by cement copper in an agitating tank. Heat by a steam jet, forming cuprous chloride: $CuCl_2 + Cu = 2CuCl$. Treat the cuprous chloride in revolving barrels with a small amount of water, scrap iron and salt (sodium chloride). The salt helps to start the reaction by dissolving some cuprous chloride: $2CuCl + Fe = FeCl_2 + 2Cu$. Evaporate the ferrous chloride solution in an iron pan. Charge the solid ferrous chloride into retorts which are provided with water (for steam) and air, hydrochloric acid being regenerated for use in the process: $2FeCl_2 + O + 2H_2O = Fe_2O_3 + 4HCl$. This modified process was used for some time until Hofmann received instructions to change the plant over to the more profitable manufacture of blue vitriol. (Greenawalt, p. 241; Mineral Industry, Vol. XVII, 1908, p. 296, Ottokar Hofmann.)

The Bradley Process.

The sulphide ore is carefully roasted at 450° C. to 550° C. in a roasting furnace known as the "amphidizer." The roasted ore is treated with calcium chloride solution in a reaction drum at 100° C., converting copper sulphate into cupric chloride, and any ferric sulphate produced by roasting is changed to ferric

chloride. The resulting calcium sulphate is insoluble. The ferric chloride which forms dissolves copper oxide, copper sulphide and metallic copper which may have remained unaffected by roasting. The gold and silver in the ore are brought into solution by adding free chlorine. The chlorides of silver and gold, soluble in calcium chloride solution, may be precipitated with the copper. After leaving the reaction drum the pulp is filtered. The solution is subjected to further oxidizing operations so as to be sure the metals are all combined at their highest valency. The solution is then in condition for treatment for the separation of the dissolved metals. (Greenawalt, p. 243; E. and M. J., Jan. 6, 1912; U. S. Patent, No. 1,011,562, Dec. 12, 1911.)

Longmaid-Henderson Process.

This process consists in roasting pyrite cinder from sulphuric acid works with sodium chloride, leaching out the cupric chloride formed and precipitating the copper by iron. Longmaid obtained patents, Oct., 1842, and Jan., 1844, relating to the treatment of pyrite cinders by roasting with sodium chloride. He may be regarded as the pioneer in the field of the wet extraction of copper. Gossage, in 1850, first used sponge iron to precipitate copper. Henderson improved the process in 1865, adding absorption towers, so that the gases from chloridizing roasting yielded weak acid, which was used for leaching copper ores. The steps in the process are: Mix the roasted ore (pyrite cinder) with sodium chloride, and grind mixture. Chloridizing roasting. Leach the roasted ore. Precipitate the silver from the argentiferous liquors. Precipitate the copper from the desilverized liquor. Prepare the leached ore for the iron works. Analysis of average pyrite cinder, 4 to 5 percent copper; sulphur, equal to or greater than copper. Mechanical furnaces use less salt than hand roasters, average 7.5 percent.

In the German works at Oker, average results showed: 75 percent of the copper soluble in water, 20 percent of the copper soluble in dilute hydrochloric acid, 5 percent of the copper insoluble. The leaching of the roasted chloridized ore was done in wooden tanks with filter bottoms of perforated boards painted with coal tar. The process was: Weak liquor from previous tank was applied, going off as strong liquor to precipitation tanks.

Then two hot washes were applied, producing weak liquor to be used again on another tank. Next, dilute tower acid was put on six times; a satisfactory extraction resulted. The acid liquors, which produce somewhat impure copper, may be precipitated separately. Copper precipitated from neutral solution is pure. Copper precipitated from acid solution is impure. Most cupriferous pyrite contains some silver and small quantities of gold. Silver chloride soluble in other chlorides, and gold chloride soluble in water, are extracted with the copper. Formerly there were various schemes proposed for the separate recovery of gold and silver from copper. Now usually there is no attempt made to recover gold and silver separately from copper, because of the cheap electrolytic method of refining copper. The residue, "purple ore," was briquetted and sent to the blast furnace. (Greenawalt, p. 246; Lunge's Treatise on the Manufacture of Sulphuric Acid and Alkali, Vol. I, 1891.)

The Longmaid-Henderson process as carried out at the works of the Pennsylvania Salt Manufacturing Company at Natrona, Pa., where 200 tons of pyrite cinder is treated per day, is: Grind to 20 mesh in Chilean mill with 10 percent of salt. Add raw ore so that sulphur equals 1½ times weight of copper. Charge 9,600 lb. mixture into the muffle roasting furnace, kept 8 hrs. at dull red heat, 800° C. Send roasted material to cooling floor, then to leaching vats. It is not desirable to precipitate silver by Claudet's iodide process, because it leaves 5 oz. silver to the ton of copper, and electrolytic refineries and blue vitriol works will pay for 95 percent of the silver and all the gold and copper. Cost to treat one ton of pyritic cinder, $1.87. (Greenawalt, p. 262; Mineral Industry, Vol. VIII, IX; Joel G. Clemer.)

The cost of producing copper by the Longmaid-Henderson process in a modern plant, using mechanical roasters: Eastern U. S., treating per day 30 tons pyrite cinder containing 2.27 percent Cu, 2.28 percent S, was 5.2 cents per pound of copper. Western U. S., under similar conditions, it was 6.5 cents per pound of copper. (Greenawalt, p. 266.)

Copper Precipitated by Chemical Reagents.

The copper precipitants used are: 1. Iron: Cast iron, wrought iron, sponge iron. 2. Hydrogen sulphide. 3. Lime.

1. Iron precipitates copper according to: $CuSO_4 + Fe = Cu + FeSO_4$; $CuCl_2 + Fe = Cu + FeCl_2$. (Theoretically, from solution of cupric salts, 0.88 lb. of Fe precipitates 1 lb. of Cu.) $2CuCl + Fe = 2Cu + FeCl_2$. (From solutions of cuprous chloride, 0.44 lb. Fe precipitates 1 lb. Cu.) Iron may be consumed by ferric salts and by free acid: $Fe_2(SO_4)_3 + Fe = 3FeSO_4$; $2FeCl_3 + Fe = 3FeCl_2$; $H_2SO_4 + Fe = FeSO_4 + H_2$. Thus for minimum iron consumption the solution going to precipitation ("cementation") tanks should be free from ferric salts and low in acid.

At Stadtberg, Westphalia, where hydrochloric acid was used for leaching, 1.27 lb. iron precipitated 1 lb. copper. In the Hunt and Douglas process, 0.5 lb. to 0.7 lb. iron precipitated 1 lb. copper from cuprous chloride solutions. At Gumeskevsky Mine, Russia, where cast iron was used both in plates and granulated, it was found that tanks charged with 12 tons of granulated cast iron, placed in layers 4 inches thick on four inclined false bottoms, gave as good precipitation as tanks charged with 115 tons of plates. Wrought iron scrap is much used.

It is often advantageous to make the iron on the spot. Sponge iron may be made by heating ferric oxide in a reducing atmosphere and cooling in a reducing atmosphere. In a measure it solves the problem of iron supply. It has long been known that iron sponge can be thus produced, but the idea has not met with much encouragement.

2. Hydrogen sulphide precipitates copper as cupric sulphide: $CuSO_4 + H_2S = CuS + H_2SO_4$; $CuCl_2 + H_2S = CuS + 2HCl$. Acid regenerated by the precipitation is returned to the ore to dissolve more copper. This does not regenerate all the acid applied to the ore; some acid must be supplied to the process.

3. Lime (calcium hydrate or milk of lime) is not suitable for precipitating copper from sulphate solutions on account of contaminating the precipitated copper with calcium sulphate. It was for a long time used with the Hunt and Douglas process, and was found to be a successful precipitant because the resulting calcium chloride is very soluble: $2CuCl + Ca(OH)_2 = Cu_2O + CaCl_2 + H_2O$. (Greenawalt, p. 270 to 282; Lunge, "Sulphuric Acid and Alkali Manufacture," p. 815.)

II. Electrolytic Methods:

The successful electrolytic refining of blister copper has turned the attention of metallurgists to the application of similar operations in the extraction of copper direct from its ores. There are difficulties in the electrolytic extraction of copper from its ores that are not met with in the electrolytic refining of copper, yet these difficulties do not appear insurmountable.

In electrolytic refining a soluble anode is used. Theoretically, there is no consumption of energy, and no acid consumed or generated. With the soluble anode there is no serious difficulty. When copper is dissolved from the ore, conditions are different. The insoluble anode is the first serious difficulty. It is hard to find a good conducting substance which is not attacked during electrolysis. Graphitized carbon has given satisfaction with chloride electrolytes, but not with sulphate electrolytes. For sulphate solutions no satisfactory anode has been found; on the whole, peroxidized lead is the best material for this purpose.

The cathodes are usually thin sheets of pure copper. In depositing copper from impure solutions derived from the leaching of ores it is found difficult to get a reguline deposit, unless considerable care is taken with purifying the electrolyte and the regulation of current density. Irregular deposition and sprouting may require the removal of the cathode before acquiring the desired thickness. With reasonably pure electrolyte and low current density, difficulty will not occur, especially if the electrolyte is agitated or the cathode oscillated. The current density and the nature of the electrolyte have much to do with the purity and the quality of the deposit.

Most electrolytic processes are based on the regeneration of the solvent during electrolysis. This requires that the anolyte and catholyte be kept separate. A diaphragm which will allow the current to pass, but prevent solutions from mixing, becomes necessary. Few materials for diaphragms fulfill all of the requirements. They must be permeable to ions, prevent diffusion of electrolyte, and carry no current by metallic conduction. Asbestos is the best material, as it is not easily attacked by acid or alkaline solutions. It is used as cloth, paper or mill board.

The current density affects the efficiency of the operation and

the nature of the copper deposited. It is not possible to use as high current density as in electrolytic refining, because of the impure and leaner solution. To get reguline deposit, operation at low current density is necessary. High current density causes impoverishment of ions at the electrodes, which may be prevented by stirring the electrolyte or by a moving electrode. Energy efficiency becomes less as the current density increases.

Wilde was one of the first to deposit copper on a revolving cathode. He secured an even distribution of the copper. The current density was 20 amperes per sq. ft. (2.2 per sq. dm.). Elmore used horizontal mandrels. The current density was 30 amperes per sq. ft. (3.3 per sq. dm.). Copwer-Coles used a cylindrical cathode, revolving at a speed of 1500 to 2000 lin. ft. (450 to 600 m.) per minute, with a current density of 200 amperes per sq. ft. (22 per sq. dm.). (U. S. Patent 895,163, Aug. 4, 1908, Cowper-Coles; Greenawalt, p. 283 to 290.)

Theoretical Data.

1 ampere-hour deposits from cupric solution, 1.1858 gr. copper.

1 ampere-hour deposits from cuprous solution, 2.3717 gr. copper.

12,000 ampere-hours deposits from cupric solution, approximately 32 lb. copper (theoretically 31.15 lb.).

12,000 ampere-hours deposits from cuprous solution, approximately 64 lb. copper (theoretically 62.30 lb.).

The theoretical voltage required for electrolyzing with insoluble anodes is: For cupric sulphate, 1.22 volts; cupric chloride, 1.35 volts; cuprous chloride, 1.53 volts.

The output in depositing copper from solutions with insoluble anodes is:

Cupric sulphate, $\frac{32}{12 \times 1.22} = 2.1429$ lb. per kw. hour.

Cupric chloride, $\frac{32}{12 \times 1.35} = 1.9364$ lb. per kw. hour.

Cuprous chloride, $\frac{64}{12 \times 1.53} = 3.4174$ lb. per kw. hour.

Illustration: There were used in precipitating copper from cuprous chloride solution 400 amperes per 12 hours (4800 ampere-hours) at 1.8 volts. Copper deposited, 18.2 pounds. Theoretically there should be deposited $\frac{4800}{12{,}000} \times 64 = 25.6$ lb.

Current efficiency, $\frac{18.2}{25.6} = 71.2\%$ (practice, about 90%).

There was deposited, $\frac{18.2}{4.8 \times 1.8} = 2.11$ lb. of copper per kw. hour.

Energy efficiency, $\frac{2.11}{3.417} = 61.8\%$ (practice, about 50%).

For electrolytic refineries, Addicks gives a rough summary of the relative value of the resistances in practice: Metallic resistance 15 percent, electrolytic resistance 60 percent, contacts 20 percent, counter E. M. F. 5 percent. The counter E. M. F. in copper refining, due to greater concentration at the anode than at the cathode, is 0.02 volt. Copper refining employs 0.2 to 0.4 volt between the electrodes. Copper depositing with insoluble anodes employs 1.5 to 3.0 volts, depending on the current density and concentration of the electrolyte. (Greenawalt, p. 295; The Journal of the Franklyn Institute, Dec., 1905, Addicks.)

The solvents usually employed have sulphuric or hydrochloric acid as the basis. The cycle consists of: Solution, precipitation, regeneration. In a cyclic process the solution is likely to become charged with impurities and reduce the efficiency of the deposition.

The injurious effects of impure electrolyte are:

1. Undesirable metals may be deposited with copper, when the solution becomes impoverished.

2. Useless energy is expended in reduction and oxidation, deposition and immediate dissolving.

The metals whose compounds have the lowest heats of formation are first deposited. Gold, silver and copper come first, and are deposited in the order given. If the current density and, consequently, voltage exceed a certain amount, several metals may be deposited together. The more neutral the electrolyte, the more likely the more electro-positive metals (such as iron, nickel and zinc) are to be deposited. High current density may deposit copper and zinc together from slightly acid electrolytes. If

much acid is present, hydrogen will be liberated, causing low efficiency. High current density may deposit copper and a more electro-positive metal not readily redissolved, producing impure copper. The practical factors which determine the kinds of ions deposited at the cathode are: Heats of formation of the constituents of the electrolyte, concentration of anolyte and catholyte, current density at cathode, temperature of electrolyte.

If arsenic and antimony were originally in the ore, they should have been largely eliminated by roasting. If they should accumulate in the solution, they may be precipitated by hydrogen sulphide, which, however, is expensive. Iron is most likely to be in the lixivium. In sulphate solutions the iron may accumulate to saturation, unless the solution is purified at intervals. With chloride solutions, more or less ferric oxide is precipitated by reaction with the ore. The influence of iron in the electrolyte may be summed up as follows:

1. Becomes oxidized to ferric salt at the anode.
2. Is carried to cathode by diffusion and circulation.
3. Dissolves precipitated copper, becoming reduced to the ferrous condition.
4. Is carried again to the anode by diffusion and circulation, again becoming ferric iron.

This cycle continues indefinitely, greatly reducing the efficiency of the electric current. To economically precipitate copper from an electrolyte containing much iron, either a diaphragm must be used to prevent diffusion, or a reducing agent (acting as a depolarizer) must be introduced.

There are two alternatives relative to impure electrolyte:

1. Purification of electrolyte.
2. Wasting a portion of the solvent, and replacing with fresh solution.

Ulke states that the best method is to electrolyze in special vats with lead anodes and to use a current density sufficiently strong to deposit arsenic and antimony, but not strong enough to deposit iron. This is repeated till the bath contains so much iron that it is necessary to remove it by crystallizing out the ferrous sulphate. (Greenawalt, p. 300; "Modern Electrolytic Copper Refining," Titus Ulke.)

Ottaker Hofmann gives the following method for purifying copper sulphate solutions containing as impurities salts of iron, arsenic, antimony, bismuth, etc.: The crude copper sulphate solution is forced into towers lined with lead and provided with a lead steam coil for heating. A lead pipe connected with an air compressor enters through the funnel-shaped bottom. When the solution is hot, roasted matte is added and air forced in, causing precipitation of the iron according to: $2FeSO_4 + O + 2CuO = Fe_2O_3 + 2CuSO_4$. To observe and regulate the progress of the operation the solution is tested for iron from time to time. When the solution is free from iron it will contain no trace of other impurities. (Mineral Industry, Vol. VIII, p. 192, Ottaker Hofmann.)

At the Kalakent Copper Works, Russia, impure electrolyte was run over dead roasted matte, then over a heap of low-grade copper ore. The neutral solution was run into a lead-lined vat, where it was diluted to 12° B. and heated to 50° C. Scrap anode copper was hung in the vat to neutralize any acid found in the operation. Compressed air was forced in till the concentration was 15° Bé., the scrap copper being quickly dissolved. The liquid was drawn off and clarified. The excess of purified electrolyte which gradually accumulated was withdrawn from the system and worked up into bluestone ($CuSO_4.5H_2O$). The copper produced was 99.9 percent pure. ("Modern Electrolytic Refining," p. 145, Titus Ulke.)

Copper sulphate may be crystallized out of impure solutions, redissolved in water and electrolyzed to deposit the copper, thereby regenerating acid which is applied to leaching the ore. The impurities are thus eliminated.

Greenawalt proposes purifying chloride solutions by electrolyzing sodium chloride, producing free chlorine and caustic soda: $NaCl + H_2O +$ electric current $= NaOH + Cl + H$. Caustic soda is applied to a portion of the withdrawn electrolyte, causing precipitation of the bases according to: $RCl_2 + 2NaOH = 2NaCl + R(OH)_2$. (R represents the base metals.) The chlorine is converted into hydrochloric acid: $2Cl + SO_2 + 2H_2O = 2HCl + H_2SO_4$. Thus the impurities are eliminated and the hydrochloric and sulphuric acid solvents are regenerated. (Greenawalt, p. 303, p. 352.)

If impurities in the electrolyte do not materially interfere with the efficiency of the process, it is better to work with impure solution even though impure copper be deposited. The efficiency of the process is more important than the relative purity of the copper.

Cobly, in 1878, described the use of sulphur dioxide for the depolarization of insoluble anodes in the deposition of copper. Its operation in recent years is common and well understood. Other depolarizers have been suggested. (Greenawalt, pp. 283 to 309.)

The following theoretical voltages were calculated by introducing Richards' thermochemical data in reactions, which we believe represent the operation of the electrolytic cells:

I. Deposition of copper from sulphate solution:

(a) Without using a depolarizer, $CuSO_4 + H_2O +$ electric current $= Cu + H_2SO_4 + O -$ 56,300 calories.

$$\text{Theoretical voltage, } \frac{56{,}300}{(96540 \times 0.24 \times 2)} = 1.22 \text{ volts.}$$

(b) Using SO_2 gas as a depolarizer, $CuSO_4 + SO_2 + 2H_2O +$ electric current $= Cu + 2H_2SO_4 +$ 7,300 calories.

$$\text{Theoretical voltage, } \frac{7300}{(96{,}540 \times 0.24 \times 2)} = -0.15 \text{ volt.}$$

(c) Siemens and Halske process, using $FeSO_4$ as depolarizer, $CuSO_4 + 2FeSO_4 +$ electric current $= Cu + Fe_2(SO_4)_3$ —16,800 calories.

$$\text{Theoretical voltage, } \frac{16{,}800}{(96{,}540 \times 0.24 \times 2)} = 0.36 \text{ volt.}$$

II. Deposition of copper from cupric chloride solution:

(a) Without using a depolarizer, $CuCl_2 +$ electric current $= Cu + 2Cl$ —62,500 calories.

$$\text{Theoretical voltage, } \frac{62{,}500}{(96{,}540 \times 0.24 \times 2)} = 1.35 \text{ volts.}$$

(b) Body's process, using $FeCl_2$ as a depolarizer: $2FeCl_2 + CuCl_2 +$ electric current $= Cu + 2FeCl_3$ —7,000 calories.

$$\text{Theoretical voltage, } \frac{7000}{(96{,}540 \times 0.24 \times 2)} = 0.15 \text{ volt.}$$

III. Deposition of copper from cuprous chloride solution:

(a) Without using a depolarizer, CuCl + electric current = Cu + Cl —35,400 calories.

$$\text{Theoretical voltage, } \frac{35{,}400}{(96{,}540 \times 0.24)} = 1.53 \text{ volts.}$$

(b) Hoepfner's process, using CuCl as a depolarizer, $2CuCl$ + electric current = Cu + $CuCl_2$ —19,400 calories.

$$\text{Theoretical voltage, } \frac{19{,}400}{(96{,}540 \times 0.24)} = 0.84 \text{ volt.}$$

In the above equations, where the minus sign (—) precedes the numerical value of the calories, this sign means that the given number of calories is absorbed in the reaction and that their equivalent in electrical energy must be supplied from an external source, *viz.*, the dynamo. Thus the calculated voltage is the necessary theoretical impressed electromotive force that must be supplied in order that the reaction may take place. When a depolarizer is used the required impressed volts are lower than when a depolarizer is not used. Compare equation I (c), 0.36 volt, with equation I (a), 1.22 volts. There is thus a saving of energy and also of expense in precipitating copper when using a depolarizer. This reducing of voltage due to using a depolarizer is realized more efficiently with low current density. The gas is then liberated at the anode at such a moderate rate that it will have a chance to react with the depolarizer, and not escape as such without reacting. In proportion as this reaction is more complete, so will the theoretical voltage be more nearly attained.

Referring to an experiment of K. Reinartz, recorded by Austin, Reinartz secured an anode efficiency of 65 percent when using sulphur dioxide as a depolarizer. Thus 65 percent of the oxygen liberated at the anode did react with the sulphur dioxide depolarizer. ("Metallurgie," 1908, pp. 202 to 205.)

Equation I (b) works out with a (+) sign for the calories and gives (—0.15) volt. This would indicate that with such a current density as to secure anode efficiency of 100 percent, if this could be realized, the electrolytic cell would no longer require an impressed voltage, but would become a primary cell. Of course, a dynamo would have to supply voltage to realize

a current of any magnitude, but the cost of operating, were this high anode efficiency secured, would be as low as that of electrolytic refining. (Mines and Methods, Aug., 1911, p. 282, W. L. Austin, Reinartz Experiment.)

1. Electrolytic Sulphate Processes.

There are two general classes of processes based on the solvents sulphuric acid and ferric sulphate. Neither of these solvents can be employed to the exclusion of the other. On certain copper sulphide ores, ferric sulphate solution has given good results without roasting. The necessity of using a diaphragm, or the introducing of a reducing gas such as sulphur dioxide when iron salts are present, has been mentioned.

Sulphuric Acid Process.

Only oxidized or roasted ores are effectively treated by dilute sulphuric acid. See equation I (a), where the theoretical voltage = 1.22 volts. The minimum voltage required is 1.22 volts. In practice 1.5 to 3 volts are employed. There is regenerated sulphuric acid in an amount equivalent to the copper deposited. This acid will only partially supply the acid required for leaching ore, because a certain amount of acid is consumed by action on the gangue. Yet electrolytic precipitation is an advance over precipitation by metallic iron, in which case no acid is regenerated. Theoretically, 2.1429 lb. copper are deposited per kw. hour. This energy efficiency of 100 percent cannot be attained, because it would require the ohmic resistance of the entire circuit to be *nil.* Fifty percent energy efficiency may be expected. When using sulphur dioxide as depolarizer (see equation I (b)), where theoretical voltage equals —0.15 volt, no power will be required theoretically to deposit the copper, and the process will be placed on a par with electrolytic refining with a soluble anode. The practical power consumption depends upon the ohmic resistance of the circuit and the current density employed. Tossizza ascertained by experiment that by using sulphur dioxide as depolarizer the necessary impressed voltage is diminished to 0.2 volt. Electrolytic refining uses 0.2 to 0.4 volt. (Greenawalt, p. 309; U. S. Patent 710,346, Sept. 30, 1902, Tossizza.)

Treatment of Ore by Braden Copper Co., Chile.

The plant consists of a modern concentrator, a smelter and a leaching plant capable of treating one-fifth of their output of concentrates. They estimated that on account of local conditions (cheap water power, etc.) the leaching of concentrates would be cheaper than smelting. The concentrates contain 16 percent Cu, 19 percent Fe and 22 percent S. The process is: Roasting concentrates; manufacturing sulphuric acid for leaching; precipitating the copper electrolytically. (Greenawalt, p. 331; E. and M. J., Dec. 30, 1911, Pope Yeatman.)

The Chile Exploration Company, Chuquicamata.

The copper in this ore exists as brochantite ($CuSO_4.3Cu(OH)_2$), which is insoluble in water, but soluble in dilute sulphuric acid. There is no arsenic, antimony or silver in the ore. The first 25 ft. of the ore body contains 0.02 percent sodium chloride. A difficulty first met was that during electrolysis obnoxious chlorine gas was given off. The process developed by A. E. Cappelen Smith is: Crush to ½ to ¼ inch. Leach in large open vats with dilute sulphuric acid. (Percolation, 16 ft. high.) Drain and wash with water. Run copper liquor, prior to electrolysis, over shot copper in order to eliminate the chlorine. The cuprous chloride thus precipitated is smelted at a low temperature with coke and lime. Calcium chloride is slagged. There is no loss of copper by volatilization during smelting of the chloride. Deposit the copper electrolytically, using insoluble magnetic oxide anodes (Fe_3O_4). There is a gain of 5 kilos of sulphuric acid per ton of ore treated. Run 8 to 10 percent of the liquor to waste. Extraction, 90 percent. This is a leaching plant which is being operated under favorable conditions. The power is transmitted from the seacoast, 41 miles distant. (E. and M. J., Oct. 4, 1913, Vol. 96, No. 14, p. 651; Met. and Chem. Eng., May, 1914, XII, p. 291.)

The Butte-Duluth Mining Company, Butte, Montana.

The ore is a decomposed granite, containing 2 percent of copper as malachite, azurite, chrysocolla and cuprite. The mining is by open cut method. The process is: Crush to ½ inch. Send to leaching tanks. Leach with 10 percent sulphuric acid solution,

put on for 24 hours. Pass liquor through the temperature cells, where it is heated to 60° C. Send heated solution to electrolytic cells. Send electrolyzed lean solution to sump, where it is standardized to 10 percent of H_2SO_4. Return the replenished solution to leaching tanks. In washing, make first water wash small in quantity, and add to mill solution. Waste an equivalent amount of the mill solution, which, prior to wasting, is run over ore till neutral, and over scrap iron to precipitate the copper. With the six new electrolytic cells, output is 100 tons finished copper (96.96 percent pure) per month. Acid consumption, 3.5 lb. per pound of copper. One pound copper per kw. hour. Cost, 13.7 cents per lb. copper. (Mining and Eng. World, Sept. 6, 1913, Vol. 39, No. 10, p. 423, Copper Leaching at Butte, Montana, Peter E. Peterson.)

Bullwhacker Leaching Plant, Butte, Montana.

The ore is from the same ore body as that of the Butte-Duluth Mining Company. The process is: Crush fine. Agitate ore with dilute sulphuric acid, using the Hendryx agitator. Separate liquor by decantation. Precipitate the copper electrolytically in circular vats, without heating, but agitating the electrolyte. Remove half the copper by electrolysis, and return the electrolyte to storage tanks for further leaching of ore. Current density, 13 amperes per sq. ft. Extraction, 90 percent. Approximate cost per pound of copper, 8 to 10 cents. (Mining and Eng. World, Oct. 4, 1913, Vol. 39, No. 14, p. 585, Bullwhacker Leaching Plant, Peter E. Peterson.)

Keith Process at Arlington, N. J.

This is an electrolytic sulphuric acid process, in which the current density at the cathode is maintained proportional to the strength of the solution in copper. The tanks cascade 128 in series. The size of the tanks and the electrode surface increase progressively as the copper content of the electrolyte decreases. The current density with 6 percent copper solution is 15 to 20 amperes per sq. ft. Voltage per cell, 1.6 volts. (Greenawalt, p. 318; A. I. E. E., 1902, S. N. Keith.)

Electrolytic Extraction of Copper from Ore at Medzianka, Poland, Russia.

This is an electrolytic sulphuric acid process using anodes which are wrapped in permeable envelopes of fabric. The thickness of the fabric is inversely proportional to the current density. Anodic oxidation of cations is prevented. Current efficiency, 90 percent; copper deposited, 0.77 lb. per kw. hour; energy efficiency, $\frac{0.77}{2.1429} = 36$ percent. (Greenawalt, p. 313; U. S. Patent No. 757,817, April 1, 1904.)

Plant of Intercolonial Copper Co., N. S., Canada.

The process is: Roast ore to sulphatize the lime and oxidize iron sulphide to ferric oxide. Drop hot ore into 5 percent sulphuric acid. Send the copper sulphate solution to storage tank. Blow in sulphur dioxide. Send reduced solution to electrolyzing tanks, which are arranged in cascade. Force sulphur dioxide into electrolyte through hard rubber tubes, which acts as agitator. The anodes were slowly sulphatized, much less rapidly than they would have been peroxidized were SO_2 absent. Current density 6 amperes per sq. ft. Voltage, 1.5 volts. Electrodes spaced 1½ in. apart. Current efficiency 90 percent. The solution enters the electrolyzer with 2.5 percent copper and leaves with 1 percent copper. The process is cyclic, continuing indefinitely. Ore contains 2.5 percent of copper, and tailings 0.1 percent. (Greenawalt, p. 316; Electrochemical Industry, Apr., 1903.)

Tossizza Process.

Ferruginous copper sulphate solutions are electrolyzed while introducing sulphur dioxide into the electrolyte. The voltage is so adjusted that copper is deposited without affecting the iron. Voltage 0.2 to 0.6 volt. (Greenawalt, p. 330; U. S. Patent No. 710,346, Sept. 30, 1902.)

Siemens-Halske Process.

The ore is ground fine and roasted at moderate temperature. It was the intention of the inventor to so roast that most of the iron would be converted to ferric oxide, while most of the copper

would remain as cuprous sulphide. This operation could not be performed. An equally satisfactory roast can be obtained when conducted at a moderate temperature (450° C. to 480° C.), most of the copper being converted into soluble sulphate. Do not roast at a high temperature (dead roast), because much cupric oxide would combine with silica to form silicate, and with ferric oxide to form ferrite, which are difficultly soluble compounds. The active solvent of the process is ferric sulphate, which should dissolve all the cuprous sulphide left undecomposed during the roasting. In the operation of this process, ferric sulphate becomes reduced to ferrous sulphate. In the electrolytic cell the ferrous sulphate acts as a depolarizer with regeneration of ferric sulphate. A diaphragm is used between anodes and cathodes. See equation I (c); theoretical voltage = 0.36 volt. In experimental tests, impressed voltage used varied from 0.75 to 1.8 volts. This process is not in practical use. (Greenawalt, p. 319.)

Experiments at the Ray Mines, Arizona, by W. Y. Westervelt.

The ore at Ray mines is a great body of disseminated sulphides. The process decided upon for the experiment was along the lines of the Siemens-Halske process. One ton of 2.5 percent copper ore was treated. Extraction, 80 percent; 1.06 lb. Cu was produced per kw. hour. Cost of copper per pound, 4.5 cents, which included only the operating expense. When charged with mining, transportation, etc., the cost would be 14.5 cents per pound of copper. (Greenawalt, p. 327; Mines and Methods, Oct., 1910, W. L. Austin.)

The Robertson Process.

The process is: Grind the ore fine. Roast at low temperature with the intention of producing a major amount of sulphates. Agitate the ore by steam, air or gases under pressure in an electrolytic tank with cone-shaped bottom, and use the proper electrolyte, usually the sulphate. The copper becomes dissolved from the ore at the anode, thereby acting as depolarizer, and is precipitated on the cathode. The solution is used repeatedly on new lots of ore. Claimed extraction, 90 percent. Current efficiency, 70 to 90 percent. Voltage, 1.6 volts. (U. S. Patent

978,211, Art of Extracting Metals Electrolytically, Dec. 13, 1910, James Hart Robertson, N. Y.; U. S. Patent 988,210, Mar. 28, 1911.)

2. *Electrolytic Chloride Processes.*

There are three general classes of processes based on the solvents hydrochloric acid, ferric chloride, cupric chloride.

The Body Process for the Extraction of Gold, Silver and Copper from Ores.

This process, patented in Belgium in 1883, is of interest historically. The ore is ground fine and roasted. It is subjected to the action of ferric chloride solution while an electric current is simultaneously passing through. The metal becomes dissolved, and is precipitated at the cathode. Chlorine liberated at the anode reconverts ferrous to ferric salt. Note that, theoretically, the effect of the ferrous chloride depolarizer is to reduce the required impressed voltage from 1.35 [called for by equation II (a)] to 0.15 volt [that called for by equation II (b)]. (Greenawalt, p. 340; U. S. Patent 333,815, Jan., 1886.)

The Hoepfner Process.

Cupric chloride, together with sodium or calcium chloride, is used as the solvent. The ore is ground fine and treated with the cupric chloride solution, which becomes reduced to cuprous chloride. The solution is then split in two streams, one passing through the anode compartment and the other through the cathode compartment. The anode stream acts as a depolarizer and becomes regenerated to cupric chloride, while the copper is precipitated from the cathode stream. On issuing from the electrolyzer the two streams are reunited and constitute the regenerated solvent, containing one-half the copper contents of the original stream. A diaphragm separates the anode and cathode compartments. Note that, theoretically, the effect of the cuprous chloride depolarizer is to reduce the required impressed voltage from 1.53 [called for by equation III (a)] to 0.84 volt [that called for by equation III (b)]. It is claimed for this process that practically 0.6 to 0.8 volt is required. This process was used at Schwartzenberger Hütte, in Saxony, from August, 1891, to

March, 1892. The results were unsatisfactory. The main difficulty appears to be metallurgical, the cupric chloride being a somewhat indifferent solvent. The question arises, "Would this process not work better on roasted ore?" (Greenawalt, p. 342).

Leaching Experiment on Keystone Ore at Miami, Arizona.

The ore contains 3 to 5 percent of copper, occurring on the surface in veinlets of chrysocolla ($CuSiO_3 + 2H_2O$) in white porphyry. It was desired to employ a process in which the solvent was regenerated and which produced marketable copper. The process used for experiment was a modification of the Hoepfner process. The ore crushed to ¾ in. (2 cm.) was first treated in a kiln, wherein it was subjected to the action of reducing gases from a small gas producer. The reduction was fairly complete, almost all the copper appearing in a metallic state in the calcined product. The lixiviant contained 5 percent of copper as cupric chloride, and 20 percent of sodium chloride. Calcined ore, 12 mesh, treated with hot leaching solution for 2 hours, gave 83 percent extraction; 60 mesh, 99 percent extraction. Electric light carbons were used for anodes. The potential employed per cell was 1 volt, with current density of 10 to 12 amperes per sq. ft. (1.1 to 1.32 per sq. dm.). One ton of copper was produced. The final washings from the leaching barrels were run over scrap iron, and the cement copper was used to reduce the last of the cupric chloride to cuprous chloride in the lixivium before going to the electrolytic cell. (Mines and Methods, Nov., 1911, p. 355, Leaching Applied to Copper Ore, W. L. Austin).

The Greenawalt Process.

The copper in the ore is dissolved by dilute acid chloride solution and precipitated by electrolysis. The acid is regenerated and augmented at the expense of sulphur dioxide and water. In practice, there is required to be supplied 2 ounces (58 grams) of salt per pound of copper extracted. Since the copper in the electrolyzer is in the cuprous state, twice the amount is deposited for a given amperage. The process may be applied to the following ores: 1. Siliceous oxidized copper ores. 2. Siliceous sulphide copper ores. 3. Copper concentrates. 4. Siliceous gold and silver ores containing copper.

Greenawalt claims that for treatment of No. 4 ores there is no other satisfactory process. If there is much iron in the ore, it is desirable to roast. Sulphide ores necessitate roasting. In treating these various ores experimentally an extraction of 90 to 98 percent of total copper, gold and silver contents has been obtained. Theoretical impressed voltage was 1.53 volts. (See equation III (a).) Copper is deposited 1 lb. per kw. hour. The estimated cost of producing copper is 2.7 cents per pound, administration expense not included. (Greenawalt, p. 349; E. and M. Journal, Nov. 26, 1910; U. S. Patent, 673,776, Oct. 25, 1910.)

The Recovery of the Gold and Silver Contents of Copper Ores.

Most copper ores treated by wet methods contain valuable amounts of gold and silver, the recovery of which is important in many cases. While the assay returns may be practically *nil,* the aggregate recovery in a year may be considerable. Utah Copper Company during the year 1910 recovered on an average 23 cents value in gold and silver per ton of ore treated.

The gold and silver may be recovered: (a) Before the copper is precipitated; (b) simultaneously with the copper; (c) by a subsequent operation.

(a) With the Hunt and Douglas process, when the leaching is done with ferrous chloride and salt solution, silver is converted into AgCl by $CuCl_2$. After reducing all copper to the cuprous condition the silver may be precipitated on copper.

(a) and (b) In Greenawalt's U. S. Patent 973,776, when there is gold in the ore he increases the free chlorine in the lixiviant, and thus both gold and silver are dissolved. Then leaching with fairly concentrated solution of base metal chlorides, dissolving both the gold and silver with the copper, the gold and silver may be precipitated prior to, or with the copper, by varying the current density.

(a) and (b) In the Bradley process the gold and silver are brought into solution, and may be precipitated with the copper, or separately.

(b) The Longmaid-Henderson process, while formerly precipitating the silver prior to copper, now precipitates them jointly, since the electrolytic refineries pay for 95 percent of silver and all of the gold and copper.

(c) In the Hunt and Douglas process, when leaching roasted ore with dilute sulphuric acid, the gold and silver are left in the residue. Silver is extracted by brine, and gold by chlorination, amalgamation or cyanidation. (Mines and Methods, Mar., 1912, p. 433, Leaching Applied to Copper Ore, W. L. Austin.)

Summarizing and Looking Toward the Future.

A number of important copper mining companies are experimenting with the development of hydro-metallurgical methods. Mr. Laist, at Anaconda, expects to produce copper for 6.5 cents per pound from concentrator tailings. There are two concerns in Butte, Montana, The Butte-Duluth Company and The Bullwhacker Company, which are producing finished copper on a commercial basis. Throughout the Southwest experimenting is being conducted. The Arizona Copper Company, at Clifton, Arizona, has been using leaching methods for treating concentrator tailings of their oxide mill for many years. The recent experiments of the Shannon Copper Company, at Clifton, Arizona, with a view to reducing acid consumption on an ore with a basic gangue, are very encouraging. The Braden Copper Company, Chile, is experimenting, leaching one-fifth of their output of concentrates. The Chile Exploration Company is extracting copper from an ore which is very amenable to leaching. Spain, Germany, England and Russia have commercial plants or are experimenting in this field.

It is said there is hardly a known chemical reaction which has not been applied. It would appear that no method of universal application is likely to be developed, that present methods will be perfected, and that the one most suitable will be selected for the particular case.

Passing the different methods of extraction in review, we may generalize:

I. Dissolving the copper.
II. Precipitating the copper.

I. (a) In completely oxidized ores, by crushing and leaching with dilute acid direct.

(b) In a mixture of oxidized and sulphide ores, by

sulphatizing or chloridizing, roasting, and leaching with dilute acid.

(c) In straight sulphide ores, by sulphatizing or chloridizing, roasting, and leaching with acid.

(d) In ores, by a modification of (a), (b) and (c), taking advantage of the solvent action of solutions containing ferric salts.

II. (a) Precipitating by chemical reagents.

1. Iron—cast iron, sponge iron, scrap iron.

2. Lime.

(b) By electrolytic deposition, with insoluble anodes of graphitized carbon for chloride solutions; and peroxidized lead anodes, or magnetic oxide anodes for sulphate solutions. (Fe_3O_4 anode, made by fusing magnetite, and casting.)

The precipitation of the copper will be:

1. From pure or purified electrolyte (one free from iron salts).

2. From ordinary impure electrolyte, using sulphur dioxide as depolarizer without a diaphragm, and securing (a) regeneration of acid solvent and (b) high current efficiency and high energy efficiency.

3. From ordinary impure electrolyte, using ferrous salt with a diaphragm as depolarizer, regenerating the ferric salt as a solvent, and securing high current efficiency and high energy efficiency.

There are two important economic considerations which alone should goad the metallurgist to future discoveries in hydro-metallurgical methods:

1. Enhancement of the life and value of a property 50 percent when the hydro-metallurgical process extracts 90 percent, as against 60 percent by the combined concentrating-smelting process, assuming equal cost per pound of metal produced in the two cases.

2. Possible treatment at a profit of certain complex mineral-

aggregates not otherwise amenable to extraction, recovering the several metals.

Articles not previously accredited: W. L. Austin's numerous consecutive articles in Mines and Methods, Sept., 1910, to Oct., 1912; E. and M. Journal, Oct. 4, 1913, Vol, 96, No. 14, p. 651, Leaching of Copper Ores; E. and M. Journal, Nov. 22, 1913, Vol. 96, No. 21, p. 962, Copper Leaching; Mining World, May 17, 1913, Vol. 38, No. 21, p. 947, Baxeres de Alzugaray, Extension of Hydro-metallurgical Industries; Mining and Scientific Press, July 19, 1913, Vol. 107, No. 3, p. 127; Mining and Scientific Press, Aug. 16, 1913, Vol. 107, No. 7, p. 252, Sulphuric Acid Leaching; Metallurgical and Chemical Engineering, 1913, p. 600, Leaching Copper Ores and Tailings.

Credit is also due to Dr. Edward F. Kern, of the Metallurgical Department of Columbia University, for kindly looking over the manuscript and offering suggestions.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

LEACHING OF COPPER TAILINGS

By Rudolf Gahl, Ph.D.

The electrometallurgy of copper is mainly hydrometallurgy, inasmuch as the electric current is used principally for the deposition of copper from its solutions. Up to the present time the application of the current has been confined to the precipitation of copper from solutions originating from metallic copper, in other words to the electrolytic refining of copper, but the application of electricity to copper solutions resulting from ores is being constantly advocated, and as a matter of fact, is being tried in several places on a small scale. The necessary basis for electrolytic precipitation of copper extracted in leaching operations is naturally a successful application of leaching methods, and from this standpoint a presentation of experimental results in this line may be justified for an electrochemical meeting, although the electric current was not used in these tests for the precipitation of copper.

The leaching of carbonate ores of copper has been attempted repeatedly, but has not been a commercial success, except in some isolated cases, as for instance in the case of the Arizona Copper Co., at Clifton, where such leaching operations have been carried on for a great number of years. The frequent failure of such attempts may have been the cause for the general distrust of leaching operations that prevailed among engineers up to a few years ago. Recently this sentiment has changed considerably and leaching plants of large size are being planned. I might mention in this connection the projected Chuquicamata plant in Chile and the Ajo project of the Calumet and Arizona, where it is intended to leach oxidized ores by sulphuric acid.

Engineers are even no longer afraid of giving their attention to the hydrometallurgical treatment of sulphide ores, as for instance the porphyry copper ores. Since the milling of these

ores has been undertaken on the present enormous scale, the gravity concentration process by which they are treated has been the subject of extensive study at the plants. And while this research work has shown ways for essential improvements which, for instance, make the concentration of ores possible that nobody would have thought of milling some years ago, it has, on the other hand, clearly defined its limitations.

The concentration process has been developed to such a state of perfection that on clean sulphide ores recoveries of 85 percent of the copper can be obtained. Unfortunately the ores that generally are called porphyry copper ores are not of this character, as they contain a considerable percentage of their copper in the oxidized state. This is undoubtedly partly due to the fact, that the limits between sulphide and oxidized ores are not very sharp or are not followed exactly when the ore is mined. On the other hand most of the ore bodies that are mined at present are to some extent altered by oxidation.

The water concentration process is, up to the present time, not able to extract copper in oxide combination with an efficiency, approximating the extraction of the sulphide copper. I believe that 30 percent is an average round figure for the extraction effected on the oxydized portion of the copper in sulphide ores. It follows, that where ores are largely contaminated with such material, no satisfactory saving can be obtained by ordinary concentration methods. A great many of the mines in Arizona and New Mexico suffer under this disadvantage (Chino, Shannon, etc.).

The natural consequence has been, that the copper mines have been looking lately towards a hydrometallurgical method to improve the copper extraction. Just where the hydrometallurgical method would come in has been a point of much discussion among copper metallurgists. In fact they are divided into two factions in regard to this question.

The one party, which we might term the radical party, is advocating attempts to discard the time-honored concentration method and to supplant it by an altogether different treatment. They suggest to roast the ore, to leach the calcines and to precipitate the copper from the resulting solution. Electrolytic precipitation is favored by many, although it is maintained by others that the

precipitation of copper from so low-grade solutions as would naturally result from leaching very low-grade ores is a problem which so far has not been solved by electrochemistry.

Among the men who propose such processes I might mention Keith, Laszczynski, Greenawalt, Smith, Wedge, McKay, Robertson, Slater, Van Arsdale, Antisell, David, Pope, and Hahn. Although replacing the concentration process by a process of the kind indicated at one of the prominent Western mines would mean a radical departure, it must be kept in mind, that similar processes have been in constant use for a long time both in Europe and in the East of the United States. The Pennsylvania Salt Mfg. Co. has produced copper in such a way for years.

The class of copper metallurgists which we may call the conservative party have confined themselves to supplementing the concentration process by hydrometallurgical methods. This can be done by leaching the concentrates which I understand is being tried at the Braden Copper Co. and by leaching the tailings. The latter is the more important, inasmuch as it adds to the extraction effected by the concentrator. To this class belongs the system of leaching worked out by Laist at the Anaconda, the tests with the Bradley process also at Anaconda, and tests undertaken at some of the Arizona mines.

It has been my task for a number of years to study the losses connected with the concentration of ores and to suggest remedies. I became convinced at an early stage, that for many ores supplementing the concentration by leaching would be the only possible remedy and, for this reason, I have made extensive experiments along the lines which I designated as conservative above. I will try to outline one of these experiments in the following:

The test was made at Morenci, Arizona, in connection with the concentrating plant of the Detroit Copper Co. The ore has the characteristics of the porphyry copper ores, being perhaps oxydized and kaolinized to a higher degree than other ores of the class. The principal copper mineral is chalcocite. Some chalcopyrite and some pyrite accompanies it. In concentrating, ores of this character behave in a typical way. The resulting sand tailings are always low in copper or can be reduced to a very low figure by ordinary milling methods, *i. e.*, regrinding and reconcentration. The slime tailings, however, are high in copper

contents, and no standard method of milling is available to reduce them materially. The existence of so much copper in them was in this case and in many other cases due to the accumulation of oxidized material in the slime. The oxidized portion of the ore has evidently a greater tendency to form slime than the sulphide portion, and as the recovery in oxide copper is very low, it is a common thing to find more oxide than sulphide copper in the slime tailings.

It was attempted in the experiments to be described to recover the oxide copper in an economical way by leaching with dilute sulphuric acid.

This may seem easy, and, as a matter of fact, it proved not to be extraordinarily difficult, but nevertheless was considered hopeless in the beginning by men of great experience in the metallurgy of copper. It is due to the confidence which Mr. C. E. Mills (at that time general superintendent of the Detroit, now general manager of the Inspiration Consolidated Copper Co.) had in the outcome, that a suitable testing plant was built in which this experiment could be made.

Successful leaching not only depends on getting the copper into solution, it depends just as well on the separation of liquids from solids and on the precipitation of copper from the resulting solutions.

In this case the second step seemed especially difficult, as the slime in question is very colloidal in character and behaves almost like clay. Filtering costs with this slime would probably have been prohibitive, not even considering the extra costs which the acidity of the solution would have imposed.

For this reason I looked towards a decantation method which would suit this particular purpose. Such method, in addition to eliminating the difficulty in question, would also offer the following advantage over filtering.

Where filtering is adopted in large-scale leaching operations, *i. e.*, especially in the treatment of gold and silver ores in connection with the cyanide process, the pulp is agitated with cyanide solution, until a sufficient dissolution of the metal values has taken place, then it is sent to the filter presses or vacuum filters, as the case may be.

It was found in preliminary copper leaching experiments, that

it is far more economical to leach in steps, *i. e.*, to leach fresh ore first with a solution high in copper and low in free acid, to replace this solution by another one lower in copper and higher in acid to finish the leaching with a solution still lower in copper and higher in free acid. This reduces the consumption of chemicals and raises the extraction. It has also another advantage when the precipitation of the copper is effected by iron, as was the case in these experiments. By bringing nearly exhausted solution in contact with fresh ore, as described, the ferric salts are transformed into ferrous salts, and the consumption of metallic iron is reduced nearly to the theoretical limit. The loss of iron resulting from the entrance of ferric salts into the precipitating plant is thereby very materially reduced. Filtering methods do not lend themselves to a repeated change of solutions.

Continuous decantation has, it seems, been originated by John Randall, of Deadwood, S. D. He evidently clearly recognized the importance of finishing the cyanide treatment of an ore with fresh solution, and developed what is called now the counter-current system of leaching. Mr. J. V. N. Dorr, of Denver, has, I believe, applied this system in several cyanide plants. If I understand Mr. Dorr right, he makes it a point in his installations to finish the leaching before he sends the solution to the decantation system. He, therefore, practices rather counter-current washing than counter-current leaching. Lately Mr. John Rothwell,[1] of Denver, has called attention to the inherent advantages of counter-current leaching in cyaniding and suggested a flow-sheet based on this system.

Randall's flow-sheet taken from his U. S. Patent 708,494, Sept. 2, 1902, is represented in Fig. 1 in a diagrammatic way. It shows only the settling tanks, S_1, S_2, S_3, the mixing tanks, one of which in the inventor's arrangement precedes each leaching tank, being left out of consideration. (See cut, page 250.)

Thickened slime enters the tank S_1, after having been mixed with solution pumped to the head of the tank. It makes two products, a spigot discharge of thick slime flowing to S_2, after being mixed with the solution pumped to the head of tank S_2 and an overflow of clear solution which is the product of the leaching operation and may be sent to a precipitating plant.

[1] Met. and Chem. Eng., 9, 439 (1911).

Settling tank S_2 makes also two products, thickened slime which goes to the next settling tank in the series after having been mixed with fresh solution entering the system and a clear overflow which is pumped to the tank ahead in the series.

In the same way settling tank S_3 makes two products, thickened slime which goes to waste and a clear overflow which is pumped to S_2, the tank ahead in the series. Only three tanks are indicated in the diagram, but the number is, of course, immaterial. It will be noticed, that the solvent fluid first enters at the last tank S_3 mixing, while fresh and strong, with the exhausted solids and then passes down through the series.

While this flow-sheet represents the characteristics of counter-current leaching, it can be improved upon for the leaching of tailings slime. The fresh acid solution (for cyanide operations the word cyanide should be substituted for acid) enters the last tank of the system, and, as a part of this acid stays with the settled pulp, this fraction of the acid is lost. There is also another drawback. The leaching power of the solution in the last tank being the highest, it is very likely that leaching may still take place in this tank. If it does, it means that some copper is lost along with the acid. For this reason a sufficient number of tanks has to be provided and great care to be exercised in the operation so that leaching does not extend to the last tank.

In the installations described in the metallurgical literature, this draw-back is frequently avoided by adding another tank or two to the system in which clear water is used for the purpose of washing the settled pulp that would result from the application of the flow-sheet, illustrated in Fig. 1.

In cyanide plants there is no objection to using solutions resulting from the leaching operations in the milling department, as the cyanide has no detrimental effect on milling machinery. Crushing in cyanide solution is in fact frequently preferred. For this reason it is possible to add the fresh water (which is required to make up for the water going to waste with the tailings) in the cyanide department and to send an equivalent amount of cyanide solution to the milling department. In the cyanide department the fresh water can be used for washing the tailings resulting from the leaching operations, and this is, as mentioned above, ordinary practice.

It is not possible, however, to do this, when leaching is carried out in sulphuric acid. The resulting solutions, being unfit for use in the mill, have to be retained in the leaching department. As new quantities of water enter the leaching department all the time, solutions would accumulate, if the attempt were made to use fresh water for washing. For this reason the barren solutions coming from the precipitating plant are essentially the only ones that are available for washing the settled pulp.

Keeping in mind, that no fresh water can be used in leaching copper tailings, it follows, that the leaching plant has to be independent of the mill and that no circulation of solutions must take place between the two. The flow-sheet of the leaching plant has to be essentially a closed circuit. The only thing to do then with solutions, as they would result from counter-current leaching on Randall's plan, would be to send them to a precipitating plant and from there, having added fresh acid, to the last tank. This would result in a flow-sheet as shown in Fig. 2.

This flow-sheet can be changed in such a way, that the objections raised against the system are obviated. Fig. 3 shows the resulting modification. Two more tanks, the number, of course, is not essential, are added to the system and serve for washing purposes. The solution discharging from the precipitating plant is sent to the last tank of the series and passes through the series of tanks in counter movement to the pulp.

Comparing Fig. 3 with Fig. 2 it is evident that there is no difference in the flow sheets except regarding the condition of the pulp at various points of the system. While in Randall's flow-sheet the fresh solution enters at the tail end of the system, the solution from the precipitating plant, low in copper and low in acid, does so in the modified system. On the way through the series of tanks, it is charged with fresh acid and continues its journey through the system. In this manner the first tanks (counting in the direction of the flow of the thickened pulp) serve mainly as leaching, the others as wash tanks.

By the way, I might call attention to the possibility of applying heat to a system like this, although no use has been made of artificial heat in the experiments made with this plant. If heat in the form of steam or otherwise is applied at the same point or near the point, where the acid is added, as marked in Fig. 3,

the temperature, after equilibrium is reached, will drop toward the tail end of the system, as will easily be seen by tracing the way in which the heat distributes itself. Accordingly only part of the heat introduced escapes with the tailings pulp, while the rest serves to preheat the inflowing pulp.

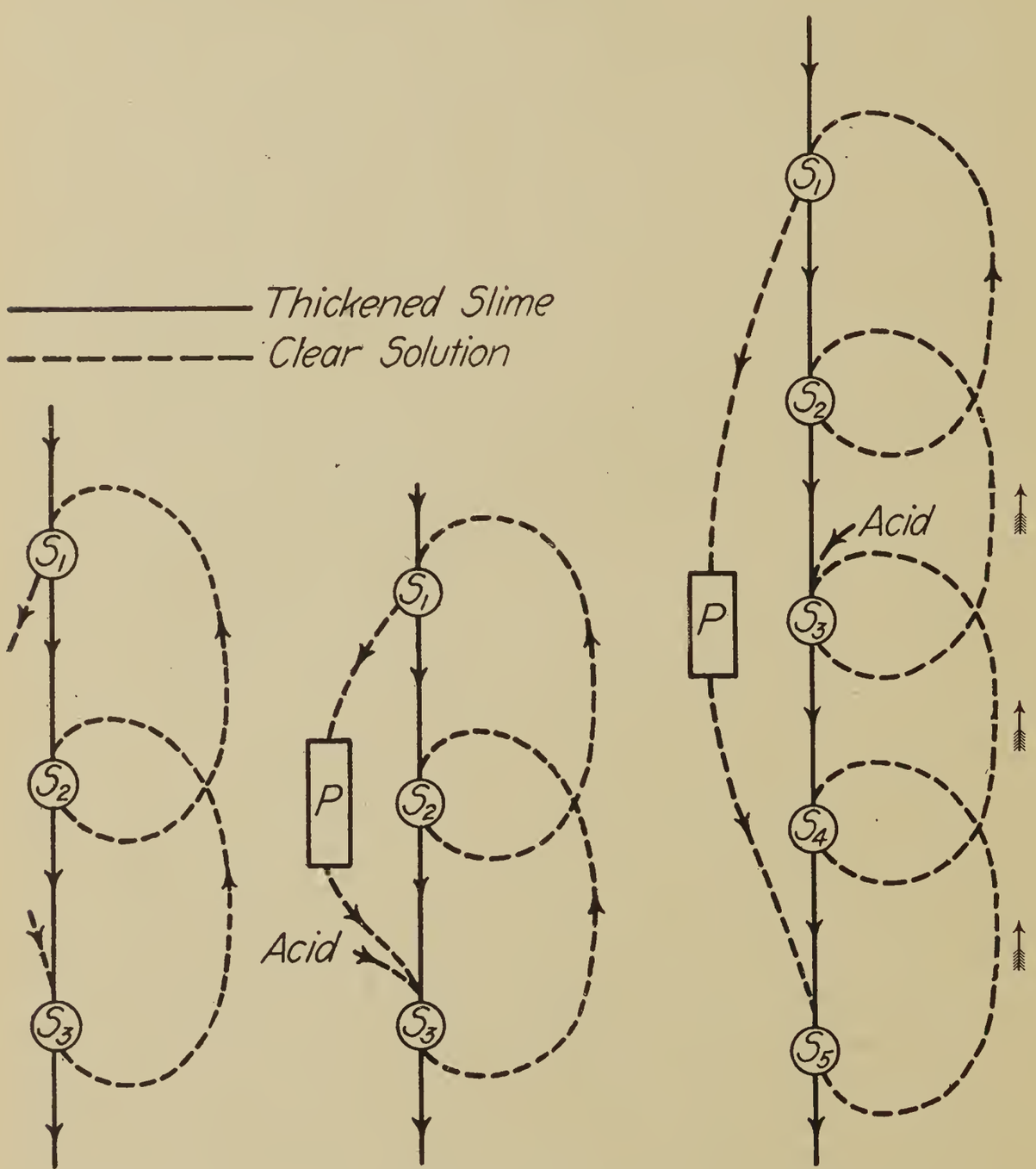


Fig. 1 Fig. 2 Fig. 3

I have been emphasizing the importance of adding acid in the most suitable place of the system. To anyone who has used similar methods in cyaniding gold and silver ores, it may seem

as if this point would not deserve so much consideration. But there is a radical difference between copper leaching and cyaniding in regard to this point.

In cyaniding there is always a large excess of the leaching agent over the quantity which is required to combine with the metal values contained in the ore. The cyanide solution charged with gold and silver will pass through the precipitating plant and emerge from it as a solution which is available as leaching liquor again. The loss in cyanide is so small, that it can be made up in almost any part of the circuit without causing much difference in the extraction. Conditions are different in copper leaching. The solution leaving the precipitating plant is useless for leaching purposes. This means, that sufficient acid has to be added to make it a solvent for copper minerals, and it is, of course, of utmost importance to add this acid where it will accomplish most good.

I will not describe in detail the plant which was constructed along the lines indicated in the flow-sheet. It may suffice to state, that it consisted of a series of ordinary settling and small agitating tanks of the simplest kind. The pulp was transferred by gravity, the solution was circulated by air-lift. A launder filled with scrap-iron served as a precipitating plant. The plant treated between 7 and 10 tons daily for a period of 50 days continuously. It was closed down only for very short intervals and only when owing to shut-downs of the concentrator the feed for the leaching plant gave out. One unskilled laborer per shift was sufficient to operate the plant; in fact, would be for a large plant, except when it was necessary to remove the cement copper and to add iron in the precipitating plant.

The conditions of the tests were varied, as far as quantity of acid and tonnage are concerned. No heat was applied. Under the best conditions a recovery of 60 percent of the copper contained in the tailings slime was obtained from material containing 1.24 percent Cu.

The 60 percent of the copper extracted represents the copper existing in the oxidized state. A higher extraction could have been obtained by using ferric sulphate in connection with sulphuric acid. Methods for cheap production of this salt were worked out in the laboratory, but have not been tried yet on a larger scale.

The probable operating costs of a leaching plant for tailings slime were calculated on the basis of the experiments, with a certain margin for safety. They are represented in Table I. The tailings slime being ordinarily a waste-product was considered not to cost anything.

TABLE I.

Probable Cost of Leaching Tailings Slime per Pound of Copper Delivered at New York.

3.50 lbs. acid @ $10.00 per ton H_2SO_4	1.75c.
1.50 lbs. of scrap iron @ $19.00 per ton	1.43c.
Power	0.25c.
Labor and repairs	1.00c.
Smelting, refining, transportation of Cu, including losses in smelting, etc.	2.00c.
Interest and depreciation of plant	1.00c.
Total	7.43c.

The figures are based on conditions prevailing at Morenci, Arizona, where the tests were made. Owing to the location of this mining camp freight rates are rather high.

Acid. The acid consumption is taken at 3.5 lbs. H_2SO_4 instead of 3.16, the figure obtained in the tests. The rate of $10 per ton of H_2SO_4 is based on the assumption, that it would be possible to obtain the acid from a near-by smelting center, where large quantities of ores high in sulphur are roasted.

Iron. The iron consumption was assumed to be 1½ pounds of scrap iron instead of 1.25 pounds pure iron. The price of the scrap iron is so high because it has to be hauled from Eastern Texas.

Power. Owing to the relatively small scale on which the experiments were carried out, it was impossible to ascertain directly the power consumption for large-scale operations. It was estimated from figures about power consumption of air-lifts and agitation found in text-books, etc. Power cost was assumed to be 36 cents per H. P. day.

Labor and Repairs. Labor for leaching was found to be, and repairs were expected to be equally negligible for a well-constructed plant. Labor and repairs in connection with the precipitation were based on what it was thought could be

accomplished in a copper precipitation plant, the operating cost figures from which were available.

Smelting, Refining, Transportation of Copper, etc. This item is based on the assumption that the smelting of the precipitate would be done in converters and includes the losses to be expected by this treatment.

Interest and Depreciation of Plant. This item is hard to approximate without making definite plans. The figure assumed may serve as an upper limit, however, and may be ample enough also to include taxes and a proportionate share of general office expenses.

As mentioned above only 60 percent of the copper contained in the tailings slime was extracted by leaching with dilute sulphuric acid, as the rest of the copper existed in the form of sulphide which is not acted upon by dilute sulphuric acid. Since making these tests the flotation process has been applied to ores of similar character and it has been found that it effects a very much higher extraction on the sulphide portion, an almost negligible one on the oxide portion of the copper. It follows, that tailings from flotation plants are lower in sulphide and higher in oxide copper. The fact has also been established that the oil used in the flotation treatment of ores does not interfere with a successive leaching of the tailings (L. R. Wallace, formerly Metallurgist, Inspiration Consolidated Copper Co.), it evidently does not attach itself to particles of oxidized copper minerals.

It seems that the conclusion may be drawn with safety that for certain classes of copper ores a combination of a flotation and a leaching process constitutes a metallurgical treatment which it will be difficult to surpass by other metallurgical processes in efficiency and cheapness.

I am greatly indebted to Dr. James Douglas, president of the Detroit Copper Mining Co. and of Phelps, Dodge & Co., for his permission to describe the Morenci leaching tests.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

METAL INVENTORY IN AN ELECTROLYTIC COPPER REFINERY.

By Ralph W. Deacon.

In any electrometallurgical plant whose products are of such value that the product losses incurred in the process form an appreciable item of the cost, it is of vital importance to the economic success of the work to be able to ascertain what these losses are, without too great an expenditure of money and without so interrupting the plant routine and production as to affect the *morale* of the organization or embarrass the selling end. In plants operating by electrolytic methods these latter present peculiar problems to be overcome in order to obtain the above results. The methods described here, as applied to an electrolytic copper refinery operating on the multiple system, can be modified to suit the conditions arising in many other kinds of electrolytic establishments. These methods have been used with success in an operating plant for a number of years, during many of which it has been under the writer's personal observation. The results obtained, viewed from the basis of a series of yearly inventories, are such as to give great confidence in their practical accuracy, while their cost is a comparatively insignificant figure in the total operating cost.

The physical inventory shows, of course, simply the amounts of the different metals on hand at a given moment, and the losses are obtained by comparing these amounts with the amounts shown as being on hand by the metal book balances. It is, however, with the taking of the physical inventory that this description deals, the remainder being a matter of bookkeeping. It might be well to say, however, before passing on, that if one would get at the true metal losses the plant must be debited with 100 percent of the various metal contents of materials received, without regard to the purchase terms.

In order to facilitate the work and bring the chance of error through omission or double accounting to a minimum, the inventory taking is divided into sections, and each major operating department is made to account for all metals it has on hand at the inventory moment or "cut off," and "cut offs" are made for both incoming and outgoing material between each of these departments. In addition there are numerous "cut offs" within each department between the various parts into which the accounting is separated.

In order to facilitate the following of the description, the plant will be supposed to be operating on the basis of the flow sheet here given, which is of a refinery using the Walker arrangement of the multiple system, and the department inventories will cover the portions of the process as indicated on the chart.

As will be seen, there are four of these separate inventories, arranged according to the stage of the process into

Anode Department Inventory,

Tank House Inventory,

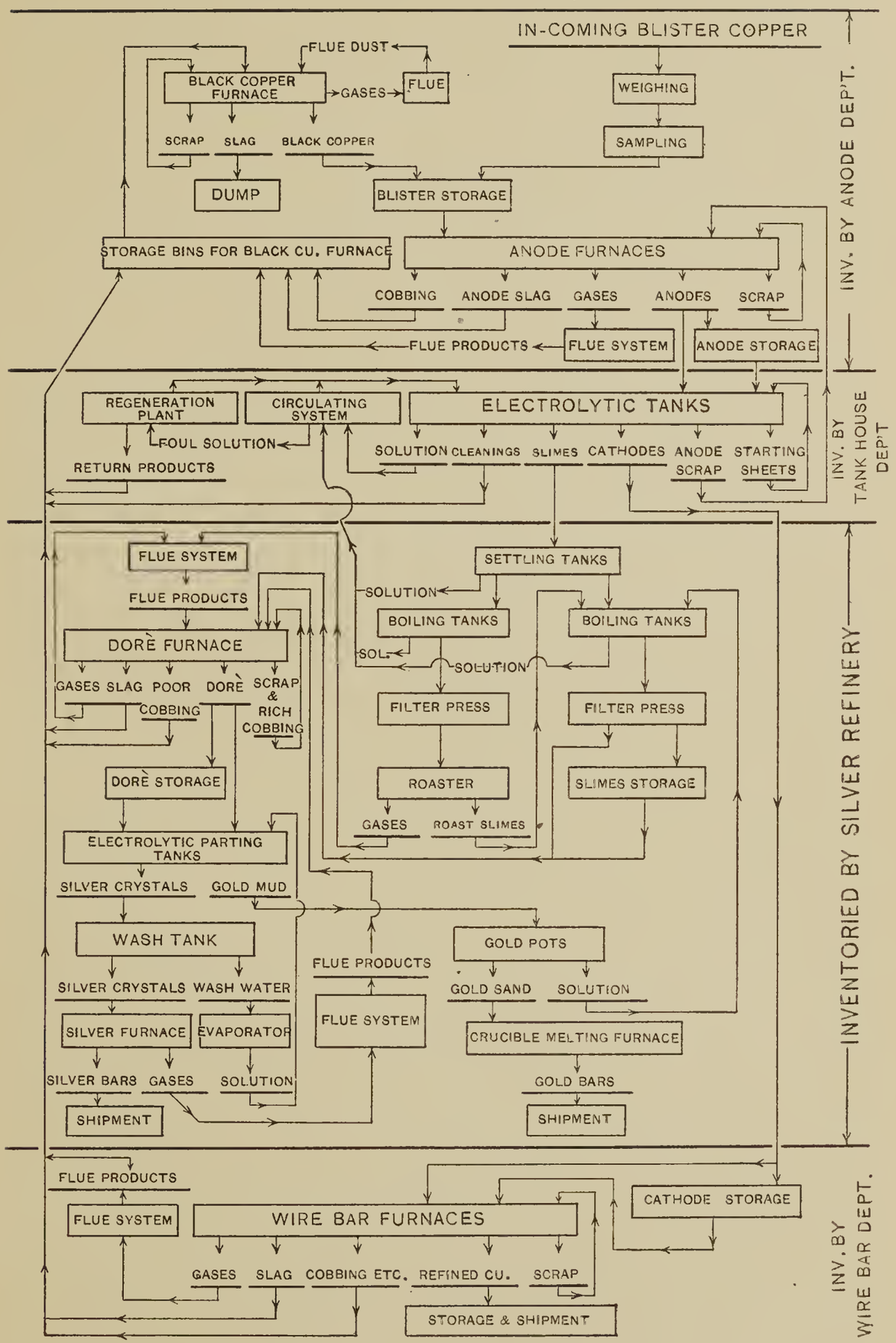
Wire Bar Department Inventory,

Silver Refinery Inventory.

In general the Anode Department accounts for all metals between the stages of arrival at the plant and delivery in anode form to the Tank House. The latter then accounts from this point to that of delivery of cathode copper or slimes. The Wire Bar Department accounts from the stage of cathodes received to refined copper shipped; and the Silver Refining Department, from slimes received to fine gold and silver shipped. Under one of the above groupings all the various steps of the process are covered, and, taken together, all metals are accounted for. The methods of accounting will be described with the idea of ascertaining only the amounts of copper, gold and silver, but other metals, such as nickel, can be accounted for at the same time if desired.

In the descriptions of inventorying the different departments, instead of following the order above, the Tank House work will be taken up first, and the Anode Department Inventory will be considered last, partly because the Tank House Inventory is the one to be first started in actual practice, and partly owing to the fact that it is found advisable for the Anode Department

FLOW SHEET OF ELECTROLYTIC COPPER REFINERY



to be made to account, in a general clean-up, of much metal from other departments that would be otherwise difficult and expensive to account for under the separate departments, and the description of this will be best understood after seeing the source of the material.

It must be kept in mind that we endeavor to look at things from an accounting standpoint, which may be at times slightly at variance with a true electrochemical point of view, but in no case is a significant error introduced.

THE TANK HOUSE INVENTORY.

The electro-deposition will be taking place under either one of two conditions, although a third condition, the division line between the other two, is possible, but not probable. Either the amount of copper dissolved at the anode will be greater than that deposited at the cathode, in which case we may consider all the deposited copper to come from the anode and the *"excess copper dissolved"* remaining in the electrolyte to enrich its original contents, or the amount of copper dissolved at the anode will be less than that deposited at the cathode, in which case we may assume that all the dissolved copper goes to the cathode and the *"excess copper deposited"* is from the electrolyte, depleting the original contents. Now, the copper in a tank at any time consists of that in the undissolved anode; that in the cathode, which then is the starting sheet plus the copper deposited from the anode and possibly plus the excess copper deposited from the electrode; and the copper in the electrolyte, which may be looked at as copper originally in the electrolyte plus the excess copper dissolved from the anode, or perhaps simply part of the former. The copper remaining in the undissolved anode plus that deposited at the cathode plus that in the slimes plus any excess in the electrolyte is the total copper originally in the anode, unless withdrawals have been made. And the copper in the electrolyte is the copper originally in the electrolyte, *i. e.*, when the anodes were charged, plus the excess copper dissolved or minus the excess copper deposited as the case may be, except for any withdrawals or additions. Therefore if we take the contents of the electrolyte before charging the anodes, and know the contents of the anodes, ascertain the contents of starting

sheet put in and cathodes drawn, keep all slimes from the anodes in the tank, ascertain the contents of the electrolyte at the time desired for the accounting, and the withdrawals from and additions to it during the period between the two determinations of the contents, then we can ascertain the contents of the tank by taking the contents of the anodes charged plus the starting sheets charged less all cathodes pulled, plus the electrolyte contents at the time, minus the excess copper dissolved which is in both the electrolyte contents and anode contents, or, as the case may be, plus the excess copper deposited, which is in neither the electrolyte nor anode items above. The original anode contents can be determined by weighing and sampling, the starting sheets charged and cathodes drawn by weighing, and the electrolyte contents by volumetric measurement, specific gravity and assay. The excess copper dissolved or deposited can be obtained by ascertaining the original electrolyte contents, to which must be added all additions, and subtracted all the withdrawals, which should give the contents at the end of the period if there had been no excess dissolving or depositing. By comparing this figure with the actual contents, the excess figure is determined and handled accordingly. Also, as there have been no slimes withdrawals from the tank, all the gold and silver content of the original anodes is present either in the undissolved anode or in the slimes, and thus can be readily accounted for.

To bring about for the entire depositing system the conditions described for a tank, the procedure is thus: On a given date, prior to the Inventory Day by a number of days slightly greater than the life of the anodes in the tanks, the electrolyte in circulation is sampled, measured and the specific gravity ascertained. From this time all anodes charged into the tanks have their contents determined by weighing and sampling; all starting sheets going into the tanks and all cathode copper pulled are weighed. Any withdrawals from the electrolyte volume, such as solution sent to the Regeneration Plant, or Silver Refinery or insoluble anode copper produced, etc., and all additions to the electrolyte such as solutions returned from the departments mentioned or copper sulfate added, etc., are accounted for by weighing and sampling, or measuring and sampling, as the case may be. Then, at the time it is desired to know the contents of the system the

electrolyte content is again determined. No accounting is made of the contents of the anodes or their products that were in the tanks when the first electrolyte measurement was made, a record simply being kept of the number of anode ampere-days that these anodes were working during the period (the use of which will be shown below) and care being taken to see that all the products, cathodes, slimes, anode scrap, etc., as the tanks are due to be "pulled" are sent out to the various departments as "old stock," and that they are entirely removed from the Tank House, except such products as starting sheets, which remain in their jurisdiction and are separately accounted for by this department.

By this method it will be seen that between the first solution measurement and the Inventory Day the tanks in the system change from those whose contents are unknown to those in which the anode contents, etc., have been determined, and, as the length of the period is slightly greater than the anode life in the tanks, all of the unknown anode products have successively fallen due for removal and been replaced by known materials. In order to prevent any of the weighed-in anodes falling due for removal before Inventory Day and thus making trouble in the accounting and the regular work by going "scrappy" and requiring "feeding," that is, replacement of anode pieces too far gone to remain in the tanks in order to balance the entire tank out to the scheduled life, the charges of anodes produced at the beginning of "weighing-in" are cast into anodes of longer life, sufficient for an extra cathode pulling, and this is continued for the necessary number of days to ensure a pulling schedule in the Tank House that will have no scrap anode tanks falling due until several days after the Inventory. As the "old stock" products are removed during this period and before charging the tanks with "weighed-in" materials, the tanks are thoroughly cleaned of all "old stock" slimes, scraps, etc., so that no "old stock" material remains in the tanks on Inventory Day, except what may be in the electrolyte.

Now we may proceed to account for the contents of the entire tank system by the same means as were used on the individual tank, since we know the original contents of the anodes charged, the starting sheets used, cathodes pulled and electrolyte contents on the Inventory Day, and so need to know only the excess copper

dissolved or deposited. As we ascertain the electrolyte contents at the start and all withdrawals and additions during the period, as well as the contents at the end, we can determine the excess copper dissolved or deposited for the entire tank system during the entire period. But this is the amount given both by unknown and weighed-in anodes during the period, of which we wish to know only the latter. All other conditions being equal, it is assumed that this excess is produced by the two in proportion to the total anode ampere-days each is dissolving, so that a similar record of ampere-days is made for the "weighed-in" anodes as for the unknown anodes referred to above; the total excess determined is then apportioned to the two, and that belonging to the weighed-in anodes is used in the manner determined according to whether it is excess dissolved or excess deposited. This, of course, gives simply the copper; the amounts of gold and silver present are, as was shown above, the contents of the weighed-in anodes, which we have determined.

In addition to this inventory of tank contents, the Tank House is responsible for all other metals in its possession, such as "old stock," starting sheets, cross-rods, bus-bars, tools, etc., that is carried in the Metal accounts instead of in Capital accounts. These are accounted for by being weighed and labeled so as to avoid duplication or being missed. Any solutions or other products on hand that have not been accounted for in the above are measured or weighed, and sampled according to the case.

As all slimes from "weighed-in" anodes are left in the tanks until after Inventory Day, prior to that time all slimes going to the Silver Refinery are of "old stock," and after the last tanks containing these slimes are cleaned the entire remaining part of the tank system is cleaned of slimes and then the system of launders, tanks, etc., through which the slimes are conveyed to the Silver Refinery. When this is completed a "cut off" is made with the Silver Refinery, in this case by means of "blanking" the pipe lines, and no "weighed-in" slimes are sent after Inventory Day to the Silver Refinery until it has passed the previous slimes sufficiently far through the process and the first part of the plant has been cleaned up to insure no mixture between the two sets of slimes. Similarly a "cut off" is made with the Regeneration plant, which, while in the Tank House jurisdiction,

still accounts for its metals as a separate sub-unit. Between the last solution sent before the Inventory moment and any sent afterwards, a complete separation is made, and the stages of the process cleaned as this line of separation moves forward, the Regeneration plant accounting for all materials on hand on Inventory Day prior to the cut off. This is done as seems most advisable from a survey made at a time prior to Inventory Day, when the condition of the plant on Inventory Day can be approximately determined. Some of the solutions may be measured and sampled as they are, and others worked up into final product shape and then weighed and sampled, the governing conditions being ease and accuracy of accounting and the necessity of so arranging the work that the minimum amount of delay will occur to the routine handling of the new solutions, etc., following after the Tank House "cut off."

These "cut offs" are made between each department and between sub-units within each department, and for materials going in each direction, and each department or sub-unit is held responsible for the proper handling of the "cut off" of both incoming and outgoing material, with especial emphasis placed on the incoming "cut off." That is, a department is not relieved of the responsibility of seeing that the "cut off" on outgoing materials is correct, but the initiative in this respect is expected to be taken by the department receiving the material, *i. e.*, the incoming "cut off." This has so worked out that any trouble due to mixup in proper "cut offs" is entirely unknown.

The "cut off" from the anode department is made after taking all the anodes from the last charge cast for delivery as "weighed-in" anodes, and no further copper is accepted until it has been accounted for by the Anode Department. The "cut off" to the Wire Bar Department is made after the last cathode delivery on the day preceding Inventory. On miscellaneous products, like anode scrap, the "cut off" is made between the last of the "old stock" and the first from "weighed-in" anodes. Step by step during the days preceding the Inventory Day the whole department is cleaned of all miscellaneous metal-bearing materials, they being either weighed and sampled or sent out to the proper department for accounting. Any material not of routine nature whose contents it is either difficult or expensive to sample

is sent out to the Anode Department for consumption in the furnaces before the Inventory Day or in the clean-up run.

The actual work of determining, recording and accounting for the metals in the Tank House Inventory is handled as follows:

To determine the contents of the electrolyte, both at the first and last measurement, all additions to or subtractions from the electrolyte are stopped and for several hours it is so circulated as to produce as uniform a mixture as possible. The sampling is then started, and samples are taken in duplicate ("in twin") at regular intervals for a stated period—about 7 hours. Uniform amounts of from 250 to 500 c.c. are taken each time for each sample. These samples are taken at a point where all solution must pass. If there is more than one circulation, separate measurements and samples must be made for each. At the end of the sampling the circulation is stopped, the solution in the launders and pipe-lines allowed to run to storage tanks, any obstruction in the tanks at the overflow removed, so that they will assume the normal level, the depth of liquor in the tanks measured and also that in the circulation tanks, wells, storage tanks and other receptacles the solution may be placed in for the purpose. The average temperature of the electrolyte when measured is ascertained. The circulation is started again as soon as this is finished and the twin samples sent to the laboratory, the measurement and temperature of solution being recorded on the sample. The laboratory, when reporting, then gives the specific gravity and assay of the solution at the measurement temperature, correcting to that from the temperature at which the laboratory work is actually done.

From the measurement data we have taken we can get the total volume of the various tanks, etc., up to the solution level, but this includes other things than solution, for which allowance must be made. Chief among these are the anodes and cathodes, etc., in the tanks, the displacement of which is considerable. This displacement can be very closely approximated by taking the weight of submerged copper and converting it into volume. We have very good figures for this weight at the second measurement, from the data taken for ascertaining the total tank contents, having only to make allowance for that portion of the anodes, etc., not submerged and for the excess copper figure. The former

can be determined by experiment, consisting as it does almost entirely of anode lugs, which will be a fixed percent of the original weight of anodes, and for the latter a percent figure can be used, being a percentage of the copper deposited, as determined by previous experience. After the excess figure is obtained by this means, correction must be made, substituting the obtained figure for the assumed one, which will probably cause a change in the obtained one, requiring another correction, etc. However, those who have performed this operation a few times will nearly always be able to so modify the first obtained figure that there will be no further change necessary, the two checking within the practical limits of error. At the first measurement the displacement must be obtained from figured conditions, which, however, as the routine work calls for weights of anodes, weights of cathodes, etc., give entirely satisfactory results, as considerable error must be made in the weights before a significant error is made in the electrolyte contents.

The contents of the "weighed-in" anodes are determined by weighing and sampling in furnace charge lots, as follows:

All anodes accepted by the Tank House from each charge are weighed on being delivered, and two types of samples taken to check against one another, the "drilled" and "splash" samples. This checking is for the gold and silver contents only, however, the drilled sample being sufficient for the copper, while the splash would not be accurate for the latter owing to oxidation of the pellets. The drilled sample is obtained by selecting an anode for a sample at the finish of casting each tank of anodes, and these are then drilled by the checker-board method, a complete template being covered. This sample is ground and quartered and prepared for the laboratory like any regular bullion sample. The splash sample is gotten by cutting the stream of molten copper as it flows from the furnace by means of a wooden paddle making a splash or a spray of shot which is caught in a pan. A splash is taken corresponding to each anode taken for the drilled sample, but, owing to the difference in location of selection, the two samples are from different parts of the charge, alternating with one another. After each splash is taken the shot are screened over a sixteen-mesh (1.5 mm.) screen, all which fail to pass being rejected. A fixed portion of the

remainder is then taken, after thoroughly mixing, and set aside with the other equal portions after previous splashes, the left-over in the pan being returned to the furnace. This combined sample, when complete, is prepared for the laboratory in much the same way as the drilled sample. The splash and drilled samples are expected to check within 1.0 oz. (0.0034 percent) in silver and 0.05 oz. (0.00017 percent) in gold. When they do not, a third sample is taken by drawing certain of the anodes from the charge in the tanks and drilling. As these anodes have been partly dissolved, only the un-submerged portion, that is, the lugs, is used for drilling, and therefore this sample is used only to determine which of the two original samples should be considered more nearly correct. Usually the samples check within the splitting limits; often the results obtained are identical. It has been customary to take the lower of the two results obtained in each case, not that this is more accurate, but from a conservative standpoint, preferring to show somewhat less than the true amount than to run the risk of showing too much. Probably a split assay would give the more nearly correct results.

In the weighing of the anodes, as in all other weighing for the Inventory, the greatest care is taken to obtain accuracy. The same methods and precautions are used as with all incoming blister, etc., and all outgoing refined copper, the material to be weighed being handled by different weighers over two separate scales in tandem, the material passing directly from one to the other, and the two scales being required to check within one pound in ten thousand pounds. The scales themselves are kept accurate by constant testing against a known weight.

Practically all the other accounting involves either a solution measurement and sampling similar to the electrolyte, a weighing of some metallic copper material according to the weighing methods described, or a weighing and sampling of some miscellaneous product, which is done according to standard methods. One exception that is noteworthy is in connection with sending the slimes to the Silver Refinery. This is pumped by a centrifugal pump and is mixed with considerable solution. It is discharged in the Silver Refinery to settling tanks, and upon settling all clear liquor possible is returned to the Tank House circulation. This liquor is considered never to have left the system, and no

accounting is made of it. There remains, however, entrained with the slimes, a certain amount of solution which is removed from the electrolyte, inasmuch as it passes along with the slimes and does not return to the circulation in its original form. In order to account for this, as it is intimately mixed with the slimes and therefore cannot be measured and sampled directly, it is assumed that the entrained solution and the supernatant solution on a tank of settled slimes have the same contents in unit volume. As they come from the same source and have just been in thorough mixture due to the centrifugal pump, this is so closely, if not actually, true as to introduce no appreciable error. A sample of the latter is therefore drawn to represent the former, and the volume of slimes plus entrained solution taken. It is therefore only necessary to determine the displacement of the slimes to get the true volume of the solution, and therefore its contents. This displacement is arrived at by weighing the slimes after filtering and by experiment determining its weight per cubic foot. If the slimes have been treated before filtering, a correction should be made for the shrinkage in bulk due to the treatment, and this can be determined sufficiently closely by experiment with a quantity of the slimes when raw and after treating.

A second exception that requires explanation is in connection with the change of anodes from "old stock" to "weighed-in," in the tanks in which starting sheets are made. At the time of pulling the "old stock" anodes the starting blanks are partly covered with copper deposited from these anodes, while the remaining copper to be deposited on them to complete the starting sheet will be from "weighed-in" stock. To separate the two, all these sheets are weighed upon being stripped, and from the records of time, current, etc., kept, the number of ampere-hours depositing is calculated for both the "old stock" and "weighed-in" copper, and the weight is apportioned to the two accordingly, the sheets being then handled as if "weighed-in" copper, and the "old stock" portion taken into Inventory.

The recording of the various items is done according to a system replete with checks to catch up any mistakes before too late to rectify them, and yet one that lends itself to easy handling.

Two records are made by the weighers handling anodes, that of the "weigher" being in book form arranged to tabulate the

weights according to furnace productions. Each record in the book, under a heading showing the production number and casting date, arranges the data in columns showing Date weighed, Car number, Gross, Tare and Net weights, Number of pieces and Load Number. The "weigher" records the loads in order as weighed, and builds up the record to a total for the furnace production. This book is retained by the weigher until the work is complete, and constitutes the original figures of Furnace Production weights. The record of the "check weigher" is in two forms, both of which he makes out in duplicate by carbon and removes from the book when complete. The first form arranges the data under the heading, "Anodes delivered to Tank House on" such-and-such date, and contains columns for Load Number, Number Pieces, Car Number, Gross, Tare and Net Weights, Production Number and Tank Number. The "check weigher" similarly records the weights, etc., for each load as weighed on his scale, and checks the net weight with the "weigher" before sending the car from the scale to the Tank House. On the anodes of each load is stamped the Production Number and Load Number. When complete this "check weigher's" form shows the weighings grouped on the form by furnace productions, with the totals for the day for each, and immediately beneath the previous day's totals, if the production is complete, thus enabling the building up of the total production to check against the totals in the "weigher's" book. Both copies of this form, as soon as completed, are delivered to the Tank House Inventory clerk. The second form is for the sample anodes, which for any production are weighed at one time. Under the heading of "Sample Anodes," with production number and date, the Car No., Number of Pieces, Gross, Tare and Net weights are recorded, and below the total for the latter appear the items "Weight of Drillings" and then "Net weight delivered to Tank House." The two copies of this form go with the sample anodes, where, after drilling, the weight of drilling is recorded and the anodes and forms delivered to the Tank House.

The first record in the Tank House is a form tabulating Tank Number, Load Number, Production Number, and Number of Pieces, and as the anodes are received and placed in tanks this form is filled out. Upon receipt of the "check weigher's" form,

Load Number, Production Number and Number of Pieces are verified from the above form and the Tank Number into which they have been placed is filled in. One copy is returned to the "check weigher" as a certification that all loads have been correctly received. The other copy is then ready for use in building up the main Tank House records. Similarly the sample anode form is checked and one copy returned to the "check weigher," from which he and the "weigher" then correct their figures for the drillings removed, getting the final net total of each furnace production.

Into a record called "Copper in Sections" the data from "check weigher's" form retained by the Tank House is then posted. This record shows Date, Section No., Production No., Number of pieces, Weight anodes, Weight cathodes drawn, Date drawn, Weight starting sheets hung, and Date, and is grouped by sections, all anodes going into tanks belonging to any one section being tabulated together, getting finally the total number of pieces and weight of copper in that section. The Weight of starting sheets hung in that section and Date are recorded, and as the cathodes are drawn, their weight and the date. This record will then show the sections in the order of their changing from "old-stock" to "weighed-in" stock anodes, and gives then the subsequent history of the section until the Inventory Day. At the end of this record is posted as "on the floor" (as against in sections) any anodes that have been received and not charged into tanks before Inventory Day, thus completing the record for all anodes received. Another record headed "Furnace Charges in Tank Room" is arranged to tabulate by Furnace Productions, the Date received, Section Number, Number of pieces and Anode weight, which is filled out by cross posting from the entries in the "Copper in Section" record. The totals of pieces and weights obtained here are checked against the production totals in the weigher's book and constitutes a check on the figures in "Copper in Sections" record. The grand totals of pieces and anode weights in these two records are also checked to verify the additions in the Copper in Sections record. From the Furnace Production record and assays is then posted the record of the Copper, Gold and Silver contents of the anodes, called "Contents of the Weighed-in Anodes." In the "Copper

in Sections" record the items of starting sheets are recorded in black or red, according to whether the sheets are "old stock" or from "weighed-in" anodes, and from this record there is cross-posted to one of "Old Stock Starting Sheets in Tanks on Inventory Day" the weights of all "old stock" starting sheets that remain in the tanks unpulled, from which a total is derived. Similarly, records for the various other items are provided, arranged according to the material, and including such items as "Copper from Insoluble Anodes Drawn during Inventory," showing date, section number, gross weight, weight of starting sheets, weight of deposit, and delivery date; "Old Stock Loops on Hand, not in Tanks," showing gross, tare and net weights; "Old Stock Starting Sheets on Hand, not in Tanks," showing the same; "Cathode Blanks on Hand," showing location, number of pieces and weights; "Cross Rods on Hand," showing same; "Triangle Rods on Hand," showing same; "Miscellaneous Copper on Hand," showing description, location and weights. The cathode blanks, cross rods and triangle rods, being constantly in use, these records have to start with the first measurement, the weighings being made as the copper is released from old stock work and before being placed in "weighed-in" tanks.

The various solution withdrawals and additions are recorded, showing date, volume, temperature, with provision for further calculation of contents.

Records are posted showing the age of anodes and cathodes in sections at time of first measurement, and also for the second measurement, and for the former, of the added age of the anodes when drawn, this being arranged by sections and expressed in tank days. Another record shows the average weight of anodes, average amperes on each circuit and corresponding number of tanks, the insoluble anodes, and the current efficiency of each day's drawings. From these the displacement figures for the first and second electrolyte measurements are calculated and the "excess copper" figure apportioned.

The records of electrolyte measurements show location, dimensions of tanks, etc., depth of liquor and volume.

The calculations have been largely covered in the foregoing, but we may summarize here that the copper in the Tank House consists of the "Copper Contents of Weighed-in Anodes" less the

"Weight of Cathode Copper Drawn from Weighed-in Anodes" plus "Old Stock Cathode Copper on Hand" plus "Weight of Insoluble Copper on Hand" plus "Weight of Miscellaneous Copper" plus "Copper Contents of Electrolyte and Other Solutions" plus or minus the "Excess Copper" item. The first item is gotten directly from the summary of "Contents of Weighed-in Anodes." The second is the total weight of cathodes pulled, obtained from the "Copper in Sections" record less any old stock starting sheets contained in them, also from the same record. "Old Stock Cathode Copper on Hand" is the summary of the starting sheet, loop, etc., stock, plus the "old stock" starting sheets in sections, plus the "old stock" copper of mixed starting sheets. The next item is from the "Copper from Insoluble Anodes Drawn during Inventory," being that portion remaining undelivered less any "weighed-in" stock starting sheets contained in them. The "Miscellaneous Copper on Hand" is a summary of all such items as cross rods, triangle bars, cathode blanks, etc. The methods of getting the "Copper Contents of the Electrolyte" and the "Excess Copper" dissolved or deposited have been previously explained.

The Gold and Silver accounted for are only from the "weighed-in" anodes, and are gotten from the summary of "Contents of Weighed-in Anodes."

THE SILVER REFINERY INVENTORY.

Upon the "cut off" from the Tank House, the Silver Refinery endeavors to return to the Tank House before the "cut off" to them must be made as much of the solution from the last slimes delivered as possible. After both "cut offs" are made, the remaining solutions are measured and sampled, and as fast as the slimes can be passed through the process the tanks, pipe lines, launders, etc., are thoroughly cleaned. As the cleaning after the slimes advances, the blocking off is moved forward between other units of the plant and the new slimes from the Tank House admitted to the first part of the process. This is continued until the entire wet treatment part of the plant is cleaned and all "old stock" slimes and other products removed to the Furnace Room, the blocking off being then made between these two units and the first part resumes operations on a normal

basis, producing pressed slimes and storing them until they can go to the Furnace Room.

Some time prior to Inventory a partial cleaning of all the flue system connected with the Doré Furnaces is made, the bulk of the values being removed, and these, together with the "old stock" slimes and other products, are worked up in the Doré Furnaces. When the last of these materials have been produced in Doré, the furnaces are "sweated out" and finally torn down. As soon as fire is dropped in the last furnace, the cleaning of the flue system is started, this time a thorough cleaning being given and the various products either weighed and sampled for Inventory, or, if there are many metallics, introducing uncertainty and difficult sampling, the material is sent out for the Clean-up Run in the Anode Department. If it is possible to do so, and this was the case in the plant where this method has been in use, a new Doré furnace in an extra position is built. Then as soon as the flues are cleaned and the new furnace is connected and all old stock material removed from that portion of the plant, the furnacing of new slimes may be started, thus saving much time.

As Inventory time approaches a survey is made and in accordance therewith, on a given charge the weighing and sampling of all Doré produced from the furnace is started. This weighing is done on bullion balances to 0.01 oz. Troy (0.28 gm.) in the same manner as outgoing Gold and Silver is weighed. This Doré is accounted for in Inventory on this weight and sample and a cut off is made between this and the previous Doré produced. This latter is fed into the electrolytic parting tanks as rapidly as possible, and as soon as the last is charged and the tanks worked down, the pieces of Doré anodes remaining in the tanks are concentrated into a few tanks and the cleaning of the others started. This is continued as far as practical, when all remaining Doré scrap is returned to the Doré furnaces to be worked up with the "old stock" slimes, and the remaining tanks cleaned. This cleaning consists of sending all gold mud to the gold plant, scraping all carbon cathodes and removing all sponge silver and silver contact pieces, and weighing and sampling the electrolyte. As rapidly as this is done the tanks are prepared again for routine work. The remainder of the plant is cleaned

up, the products going either to the silver furnace to be melted to fine silver, or back to the Doré furnace. When the cleaning of the plant is complete, the Gold Plant is blocked off and the weighed and sampled Doré admitted to the plant, which again starts on routine work. The Gold Plant works up the remaining gold mud and sends out the gold sand to be melted and shipped. The solutions are returned to the slimes boiling tanks, the starting of the Doré sampling being so timed as to have the Gold Plant finish up before the Slimes Plant completes its work. The Gold Plant is then thoroughly cleaned and the products sent to the Doré furnace for working up, the Gold Plant then being put back in normal work. All the gold or silver shipped on or after the Inventory Day from these products is taken into inventory as shipped. When the last sponge silver is melted, the silver furnace is torn out and all metallics obtained sent to the Doré furnace; the brickwork containing values or furnace cobbing is crushed fine and sent out to the Anode Clean-up Run. When the last Doré charge in a furnace is cast it is wrecked and the metallics returned to another Doré furnace until the last is torn out. The cobbing from the Doré furnaces is treated as that of fine silver furnace, the poor cobbing being weighed and sampled, and the rich cobbing being crushed fine, all metallics possible removed and then sent out to the Anode Clean-up Run. All the metallics from the last Doré furnace are melted in a crucible and cast for weighing and sampling. This constitutes the method of inventorying the Silver Refinery, there being also the accounting for any miscellaneous items not in the above routine.

The records here show the fine silver and gold from old stock materials shipped after the Inventory Moment, the contents of weighed and sampled Doré lots, the contents of the metallics melted, the contents of the lots of poor cobbing weighed and sampled, the contents of the various flue products, the contents of the solutions in the Slimes Plant, the contents of silver electrolyte and any other solutions there may be, and then the miscellaneous items, such as copper tools and bus-bars, silver contact pieces, fine silver and gold samples, etc. There is nothing special about the methods of recording or calculating these items, all proceeding along the lines of standard practices, the key note of

the inventory method in this department being the program laid out from the survey which enables each clean up to come at a time when its difficult products can be handled by the part of the process as described and yet so as to cause no great delay in the process work. The sampling of Doré must start so that the Gold Plant can get its solution to the Slimes Plant, and the Parting Plant and Gold Plant their scrap and products to the Doré furnace, so that the last "old stock" fine silver is melted so that the metallics from the silver furnace can get into the Doré furnace, and yet so that the new fine silver and gold will not be produced before Inventory Day or before the new fine silver furnace can be put to use, due to the working of the old Doré furnace, etc. If this program is not laid out properly, the comparatively simple items given above as constituting those in the Silver Refinery Inventory may have added to them some items that are either difficult or expensive to handle, or the plant may at some point be so held up as to seriously delay the delivery of gold and silver at some following period. The cobbing lots, etc., that are sent for the Anode Clean-up Run are recorded by lot and weight, but are otherwise not handled in the inventory accounting of this Department, being used to check with the records of the Anode Department of the Clean-up Run.

THE WIRE BAR DEPARTMENT INVENTORY.

For some time prior to Inventory Day the cathodes as delivered by the Tank House to the Wire Bar Department are partly diverted to stock, the amount depending on the cathode stock then on hand and the probable amount there will be on Inventory Day. These cathodes are check-weighed, listed, and the weights marked on each load and then striped with paint, meanwhile those in stock are drawn on for the furnace use so that on Inventory Day the latter have all been used. If any of the weighed cathodes have to be used for the furnace, they are listed opposite the original listing as withdrawn from stock, so that the double listing shows by difference those that are on hand on Inventory Day, when the record is checked against the actual stock, and the total amount of cathodes built up from the listing. A similar method is used for moulds and cores. The copper moulds, made of refined copper, are check-weighed as produced and each

stamped with its weight and production number. Before inventory the mould stock is culled over and any moulds that show possibility of having changed in weight are set out to be fed to the furnaces before Inventory. The remainder are listed as the cathodes were; those discarded are replaced by new ones which are listed as made. Any withdrawals after this date are handled like the cathode withdrawals, and the stock checked and amount on hand built up in a similar manner. The cores are handled in a like manner. All miscellaneous refined copper on hand is weighed and listed as to what and where, as in any stock taking. The charges of molten copper in the furnaces on Inventory Day are accounted for as they are produced, all products being weighed, including bad production, etc. After casting and charging, the furnaces hold over the following day so that everything around the rings, boshes, etc., can be thoroughly cleaned up as well as the boiler and flue systems. These things are accumulated in similar products, listed, and then weighed and sampled for accounting. Should there be enough "old stock" material on hand unweighed or unaccounted for to warrant more furnace charges than those cast on Inventory Day, a furnace may be held to work up this material, the products being accounted for as produced and the clean up made after these charges have been finished. The slag from these furnaces on Inventory Day is accounted for by weighing and sampling.

The absorption of metals in these furnaces cannot be determined by destruction, as was that of the Doré furnaces, as the expense for each furnace would be double the entire cost of inventory and the time involved prohibitive. We must therefore assume the absorption, and after this has once been done the error in subsequent inventories is reduced to a minimum, as the item is introduced into both sides of the account. When a plant has been operating for some years, if each time any large repairs or replacements on a furnace take place an inventory is made of the contents of the portion torn out and corresponding notation and description made of what this represents, good and reliable data will be accumulated from which the absorption can be fairly closely estimated. A study of these data will lead to the formulation of certain rules for guidance, but there are so many influences that go to make up these rules that may differ in

intensity in different plants, and therefore produce different sets of rules, that this phase of the matter will not be treated in detail. The study of furnace absorption could well fill a book in itself.

The refined metal in stock awaiting shipment may vary greatly according to conditions. As it is produced it is made up into shipping lots, weighed and marked. A refined stock record is kept as a regular plant record, and it is only necessary to prove that this record and the actual stock correspond, to determine the amount on hand. The refined stock is piled in certain definite places in the plant, and a plotting of these piles is made on tracing paper, showing simply a square to designate each pile, the lot numbers being marked on each square, and then the whole plotting on each sheet being referred to fixed positions such as buildings, etc. These diagrams are then blueprinted and the piles numbered on the prints, and a checker's list is made to correspond with each one. Two checkers with a blueprint and list then go over the stock identifying the items on their list from the corresponding number on the blueprint, and after verifying the lot number and location they make a count of the pieces of each lot in the pile in question and record this on their list, and the piles are then marked as having been inventoried. After each sheet is completed by the two checkers these lists are checked against one another; any discrepancies between the two are immediately investigated and corrected, and these lists are then ready for verification against the stock record. While the checking is being done the refined stock is posted from its record to a form showing in columns—Diagram Number, Pile Number, Lot Number, two columns for Number Pieces, Kind and Weight, this posting being made into the column for Lot Number, second column for Number of Pieces, and the columns for Kind and Weight. As the checkers' sheets are received these are posted into the columns for Diagram Number, Pile Number, and the other column for Number of Pieces, these postings being, of course, guided by the lot number and the kind, which also appears on the checker's sheet. These are verified with the other posting before entering the Diagram Number, Pile Number and Number of Pieces in each case. As one lot of copper may be piled in several places, there will usually appear several items to be

cross-posted from the checkers' sheets to the corresponding refined stock listing. When this cross-posting has been completed the column for Number of Pieces, as posted from the checker's sheet, is summed for each lot, and checked against the number of pieces entered in the adjoining column. Any variation is investigated and adjusted if possible, and the stock as posted and as checked brought into accord, this being kept up for all new refined product made up to Inventory Day. If any lot as posted from the stock record, and as checked, cannot be brought into accord, this lot is then picked up and reweighed, this weight being taken for the inventory weight. All lots that check are accepted on the basis of the weight in the refined stock record. On Inventory Day the original diagrams, which are kept posted up to date with any changes, are taken and checked against the stock on the ground by piles, to verify the correctness of the plotting and changes that may have been made due to withdrawals for shipment or additional product made after the original plotting. These original sheets are then checked against the tabulation of stock, and all lots on the latter not appearing on the former are thrown out. As the tabulation is also kept posted for all additions and withdrawals from the refined stock record, there should be no discrepancy between the original diagram as finally checked and the tabulation, and during my experience with this method this was the case. The refined stock is then built up by summation of the checked lots in the tabulation, and the bringing together of these various items into a summary completes the Wire Bar Inventory.

ANODE DEPARTMENT INVENTORY.

In the Anode Department Inventory is included the Blast Furnace for working up slags, etc., and this is the first work done in this Department. A survey is made of the materials on hand for smelting, and a program arranged, certain materials being held in original lots, weighed and sampled, and taken into Inventory in this manner. All other material is then worked up, and the furnace finally blown down on completing the run, and a clean up similar to those at the other furnaces made. All the pig produced prior to Inventory Day is handled as any other incoming blister. Any made on or after the Inventory Day is

listed, weighed and sampled, and taken into Inventory thus. The material held in original lots is kept separate and properly marked and watched to avoid any portion being used in the "old stock" run in the blast furnace. Should any lot be gotten into by mistake, the entire lot is used or the remainder weighed and sampled. The items therefore appearing for this portion of the Anode Inventory are contents of intact lots, and contents of pig produced after Inventory Day, and the clean up items. The absorption in the furnace bottom here may be treated as the Doré furnaces or as the refining furnaces, the former being more desirable as the absorption at different times varies much more than in the refining furnaces, and therefore is more difficult to estimate, but then it is also of much less total contents.

During the night preceding Inventory and on Inventory morning all lots of blister, etc., received at the plant and not yet gone into process so as to change their original contents, are listed, the kind, number of pieces, weights, etc., being shown, as well as location, and any that have been removed from the freight cars or lighters are striped with a distinctive paint (white). All these lots after verification are taken into inventory on their original contents. All lots that have been broken into are set to one side and striped with another distinctive paint (red), and held for the Clean-up Run. All "old stock" anode scrap is similarly striped (red) and set to one side, while all scrap from "weighed-in" stock is striped with the paint designating it has been accounted for (white), as it is sent out from Tank House until after the Clean-up Run is completed.

The charges in the Anode Furnaces on Inventory Day are accounted for by weighing and sampling the anodes as produced, and, after casting, these furnaces hold over and clean up similarly to the Wire Bar furnaces. All slag and other similar products up to and including what is made from the charges on Inventory Day are weighed and sampled. All miscellaneous material is handled as in the other departments.

This then leaves us with only the materials set aside for the Clean-up Run to account for. These materials have been carried by memoranda in the departments from which they have originated, including the Anode Department, and from these data a list showing the particulars regarding each material is made up

by those in charge of the Clean-up Run, and this is checked against the material which is accumulated in a designated place.

Estimated contents are assigned for each material, and the total to be accounted for approximated as a basis for the program to be laid out. This will undoubtedly show a scarcity of copper to carry the amount of silver and gold present, as it is desirable that the grade of the anodes be not very much greater than normal. The number of furnace charges necessary is then determined from these data to give the proper grade and the schedule of the Clean-up materials to go into each charge laid out. The remainder of each charge is then made up of "new stock" blister, the lowest in precious metal contents being chosen so as to allow for the greatest absorption from the clean-up material. Only complete lots of "new stock" blister are used, but it is not necessary to have these complete with each furnace charge, but only for the entire run. The clean-up materials are checked off as charged, and nothing but these and the "new stock" blister is allowed to go to the furnace except scrap made from these charges themselves. The output of the furnace for the run should then be the contents of the clean-up materials plus the contents of the "new stock" blister used, and as the latter is in complete lots, whose contents have been determined on arrival, we can obtain the contents of clean up materials by subtracting the "new stock" material from the total output of the furnace during the run. This latter is obtained by weighing and sampling the anodes as cast, the slag as produced, and at the end making a clean up, as on Inventory Day, of the flue system, ring and boshes.

VERIFICATION RECORD.

All the foregoing work is done by the various department men in charge of the Inventory in their respective Departments. On Inventory Day (the Inventory moment is usually 7.00 A. M.) all work stands still until the officials in general charge of the entire Inventory have made a survey of conditions and satisfied themselves as to the correctness of the Inventory. They cover the entire plant, making memoranda in the Verification Record and accompanied in each Department by the man in charge of that work. All the records as compiled are inspected and notes made on those still to be prepared, and as each section of the

plant has been covered it is released and again starts on normal operation.

As the record work in each Department is completed it is turned over to the general office for compilation, and this latter is finally verified from the Verification Record made on Inventory Day.

The writer does not consider that this is the only method to use, but simply a satisfactory method that has given good results, and will welcome any suggestions that will tend to improve the methods used, or any descriptions of substitutes.

British America Nickel Corporation, Ltd.,
Sudbury, Ontario, Canada.

A paper read at a Joint Meeting of the New York Sections of the American Electrochemical Society and the American Institute of Mining Engineers, in New York City, Nov. 20, 1913, and called up for discussion at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

THE ELECTROLYTIC DEPOSITION OF ZINC.

By J. W. Richards.

The amount of scientific and technical work which has been put on this subject is scarcely appreciated by those who have not looked extensively into its history. The German book of Emil Günther, "Die Darstellung des Zinks auf elektrolytischem Wege,"[1] covers over 250 octavo pages. There is no corresponding treatise in English, but condensed accounts of the subject may be found in recent works on electrometallurgy, electroplating and applied electrochemistry.

Günther makes the following classification of the subject:

A. Electrolysis of Aqueous Solutions.

I. *Processes using soluble anodes:*

(*a*) Refining of impure zinc used as an anode.
(*b*) Obtaining of zinc using zinc compounds as anode.
(*c*) Obtaining of zinc using soluble anodes containing no zinc.

II. *Processes using insoluble anodes:*

B. Electrolysis of Fused Zinc Salts.

Günther describes

5	processes	under	A I *a*
6	"	"	A I *b*
10	"	"	A I *c*
39	"	"	A II
8	"	"	B

It therefore appears that a very considerable amount of time and money has been spent in investigating and developing this

[1] Knapp, Halle, 1904. Price 10 Marks.

subject. The treatment of mixed zinc, copper, lead sulphide ores to obtain their zinc values has been one of the chief stimulants to this great activity; the extraction of zinc from roasted pyrites (pyrites cinders) from sulphuric acid manufacture, before passing them on to the blast furnace, has been another attractive field, while the refining of galvanizer's dross and the de-zincing of galvanized iron scrap has been another interesting subject—all these in addition to the main question of treating ordinary zinc sulphide ore in competition with the ordinary method of zinc metallurgy.

Dr. Victor Engelhardt, chief engineer of the electrochemical division of the Siemens & Halske Company, Berlin, was expected to present this subject to you tonight, but, since neither he nor his paper has arrived in time to appear on the program, I have consented to act as his substitute—on rather short notice. Under these circumstances it may be in place to reproduce the main points brought out by Dr. Engelhardt in a lecture on this same topic, delivered about one year ago, before the first general meeting of the Gesellschaft Deutscher Metallhütten- und Bergleute, in Düsseldorf, adding thereto such observations as have come within my personal experience and which are not covered in Dr. Engelhardt's lecture.

Dr. Engelhardt subdivides the subject slightly differently from Günther, and confines his discussion to electrodeposition from aqueous solutions, of which he makes two main divisions, with two and four subdivisions respectively:

I. Refining of impure zinc:
   - (*a*) Precious metals absent.
   - (*b*) Anodes containing precious metals.

II. Direct extraction of zinc from its compounds:
   - (*a*) Using soluble anodes containing zinc compounds.
   - (*b*) Using soluble anodes containing no zinc.
   - (*c*) Using insoluble anodes, but utilizing the electrochemical reaction at the anode.
   - (*d*) Using insoluble anodes and not utilizing the electrochemical reaction at the anode.

I. Refining.

(*a*) *Precious metals absent.* Dr. Engelhardt considers this proposition, where no part of the expense is compensated by the collection of gold or silver, as commercially hopeless, and dismisses the subject.

The author wishes to add, however, that technically the proposition is perfectly possible, and that it is only the absence of the values of gold and silver and the low price of zinc which render it economically unprofitable, or, rather, so little profitable as to offer no commercial attractions.

There is a large amount of impure zinc on the market, known as galvanizer's dross, which is the mushy ferruginous alloy taken from the bottom of galvanizing pots. This metal carries practically no gold or silver, but runs 90 percent of zinc, with impurities usually 5 to 6 percent of iron, 1 to 3 percent of lead, and sometimes up to 2 percent of tin. Its market price is usually 70 percent of that of commercial zinc, which leaves about 20 percent of the price of commercial zinc as a margin for refining and profit. At the present price of zinc this would be $25 per ton, but at lower prices of zinc it would fall to $18 per ton. It would appear that a commercially profitable process would have to refine this material for about $15 per ton or less to offer inducements to justify the erection of an electrolytic refining plant. Further, as compared with refining copper, it must be remembered that the expenses and difficulties in refining zinc are greater, and the margin usually less, with nothing to credit to values of precious metals recovered.

The writer conducted some extensive experiments on this process some years ago, with the following results:

The zinc dross was melted in iron pots, allowed to stand at a temperature just above its melting point, and a considerable proportion of its weight carefully skimmed from the surface as commercially pure spelter. About 25 percent of its weight was thus recovered directly as salable metal. This left the residue more impure than at the start, with a higher melting point and not so fluid. When cast into anode moulds directly it showed a tendency to liquate and also to swell up in the moulds. This was entirely overcome by raising its temperature to low redness

and adding about one-tenth of one percent of aluminium. The metal then cast into clean, smooth anodes of quite uniform fracture and structure.

Anodes 1 to 1½ inches (2½ to 4 cm.) thick and 18 x 48 in. (45 x 120 cm.) were hung in the refining baths at an average distance of 1½ inches (4 cm.) from the cathode plates. The latter were of similar surface, but of rolled zinc plates 0.25 inch (0.62 cm.) thick, greased on their surfaces to prevent adhesion of the deposit, and with the edges painted with black asphaltum varnish to prevent deposition thereon. The "greasing" was done at first with wax dissolved in methyl alcohol, but afterwards glycerine, rubbed on with a soft rag, was found to be quite satisfactory.

The electrolyte contained 15 percent $ZnSO_4.7H_2O$, 1.7 percent of acetic acid (commercial) and 0.8 percent of sodium acetate. Specific gravity 1.10. Specific resistance 31¼ ohms, at the working temperature 85° to 90° F. (30° to 32° C.). Voltage drop per tank 1.25; current density 9 amperes per square foot (100 per square meter).

Under these conditions plates would work smoothly and give good deposits for 3 to 4 days; some were good at 6 days, but many were spongy. If the plates at 3 days were lifted out and all trees carefully removed from the edges, they would then run to 6 days and give clean plates. The trees rob the rest of the plate of current, and so apparently increase the tendency to sponginess. The weight of metal obtained was the theoretical weight for 100 percent ampere efficiency when the plates were bright; spongy deposits showed usually 80 to 90 percent deposition, the loss being either from hydrogen evolution or from spongy zinc dropping off and falling to the bottom of the tank. The losses in melting down the stripped and dried deposits were large, being 20 to 25 percent of the net weight of the plates. This was diminished by using ammonium chloride (sal-ammoniac) as flux when melting down, but the expense was considerable. (It will be seen later that Dr. Engelhardt has greatly improved the melting-down operation.) The zinc obtained averaged 99.95 percent pure.

The electrolyte quickly became impure from ferrous sulphate dissolved at the anodes. As it accumulated it was necessary to

devise a plan for its removal in order to keep the electrolyte in fit working order for depositing pure zinc. Since active circulation of the electrolyte was also necessary, the plan adopted was to aerate the solution by air injected into the tanks through rubber hose, and to allow a good current of electrolyte to flow in and out of each tank. The outflowing liquid was brown from precipitated hydrated ferric oxide, and ran to a filtering tank, where the precipitate was filtered out; the clear solution was stored in a tank which contained a quantity of slabs of zinc dross, to neutralize its free acid. Another possible way of removing the iron would have been to agitate it with zinc oxide (zinc skimmings or roasted zinc ore), but this was not tried.

The net results of about two months' experimenting was to show that the electrolytic refining was practicable, but that the cost was nearly equal to the economic margin which then existed. The margin for profit was too small to justify the erection of a commercial plant, since a fall in the price of zinc might have wiped out entirely the margin for profit. It is not impossible that, under other commercial circumstances, with cheap power at command and with high market values of zinc, the electrolytic refining might offer prospects of fair profits.

I. Refining.

(*b*) *Anodes containing precious metals.* The zinc scums from the Parke's process for desilverizing lead contain ordinarily 50 percent or more of zinc, with 10 to 30 percent of lead, 5 to 10 percent of copper and 5 to 10 percent of gold and silver. By using aluminium rather liberally in the desilverizing pot (0.2 to 0.5 percent in the zinc used) the zinc scum comes off much cleaner from lead, and skimmings are obtained carrying 70 to 80 percent of zinc, 2 to 5 percent of lead, 5 to 10 percent of copper and 5 to 15 percent of gold and silver. These may be granulated and placed as a horizontal-lying cathode, or cast into plates and placed vertically. Roessler and Edelmann, at the Hamburg Gold und Silber Scheideanstalt, used zinc sulphate solution as electrolyte, current density 80 to 90 amperes per sq. m. (7 to 8 per sq. ft.), potential drop 1.25 to 1.45 volts. Although operated for some years, this process is now said to be abandoned, not being able to compete with the improved distillation and cupellation processes.

II. Direct Processes.

(*a*) *With soluble anodes containing zinc.* A great many attempts have been made since 1880 to prepare compound conducting anodes, incorporating into them various zinc compounds or ores, or roasted ores, or skimmings, mixed with coke or charcoal and binding material, and compressed or baked into solid conducting anodes. None of these have been commercially successful. Marchesi tried to work a similar idea for copper, using copper matte as anode, but, although the conditions were more favorable than with zinc ores, he finally abandoned it after several years' running.

(*b*) *With soluble anodes free from zinc.* These are usually based on using iron as the soluble anode, with diaphragm cells, so as to keep the ferrous sulphate formed at the anode from mixing with the zinc-bearing solution in the cathode compartment. These were only moderately successful from a technical standpoint, while the cost of the iron dissolved was a great obstacle to making the process commercial.

(*c*) *With insoluble anodes, utilizing the anode reaction.* Although the anode may be unattackable, yet the perducing influence of the anode reaction on the electrolyte is often useful and utilizable. The two processes of Siemens & Halske, 1886 and 1896, were based on this principle, the zinc-bearing solution from leaching the ore being first passed through the cathode compartments of a series of cells, where most of its zinc was extracted, and then passed through the anode compartments of the same cells, where the ferrous sulphate which it contained was produced by the anodic oxidizing influence to ferric sulphate. In their second process normal aluminium sulphate was changed into sub-sulphate while leaching zinc oxide, the zinc extracted in the cathode compartments, and the aluminium sub-sulphate produced to normal sulphate in the anode compartments. These processes were commercial failures, mainly because of the complications of the diaphragm cell, and are now only of historical interest.

(*d*) *With insoluble anodes, and not utilizing the anode reaction.* Several processes in this group have reached extensive commercial application.

Hoepfner used zinc chloride as the electrolyte. He established and operated plants in Germany, England and Austria, but they are no longer in operation. Günther devotes 73 pages to describing the Hoepfner process. The raw material used was the zinc-bearing pyrite cinders, containing about 10 percent of zinc, mostly as ZnS. This was given a chloridizing roasting with salt, leached, the Na_2SO_4 frozen out, oxidized by bleaching powder, precipitated by $CaCO_3$ and next by zinc dust, and the purified solution electrolyzed in a diaphragm cell using carbon anodes. Zinc of high quality was produced, but the process was too complex and the by-products were too numerous, producing a difficult commercial situation.

The Siemens-Halske sulphate process dispenses with diaphragms and rotating cathodes, and therefore affords a process much simpler in many respects. Zinc is obtained in a sulphate solution by various metallurgical methods, the solution is purified before electrolysis by bleaching powder, carbonate of lime, zinc oxide or zinc dust, and then electrolyzed with unattackable anodes. The finding of suitable anodes and the melting down of the deposited zinc without loss have been the *cruces* of the process, to which Dr. Engelhardt and Dr. Ferchland have given much study.

Acheson graphite is satisfactory as anode in chloride solutions, but it disintegrates in sulphate solutions. Platinum is too expensive and also slightly dissolved. The coating of PbO_2 forming on lead anodes is not sufficiently continuous to prevent further corrosion of the lead, followed eventually by disintegration.[2] Dr. Ferchland precipitates PbO_2 electrolytically from a proper solution on carbon tubes used as anodes, placing colloids in the solution to make a smooth deposit. After forming to the desired thickness, the anode is removed and the carbon tube bored out, leaving the PbO_2 tube. Several of these are connected together to a single anode by casting lead around them.

At a small plant in operation at Lipine, in Silesia, the zinc ores are leached in open stirred tanks. On electrolyzing with

[2] Lead anodes last longer if they are given their first coating of peroxide in an alkaline solution, and then transferred to the acid bath. While lead anodes ordinarily disintegrate within a year, they last twice as long if given the preliminary alkaline treatment.—J. W. R.

the PbO_2 anodes, zinc is deposited, running between 99.955 and 99.984 percent pure. Ampere efficiency 80 percent. Potential drop per cell 3.8 volts. Specific power consumption 3.4 kilowatt-hours per kg. of zinc, or under ½ kw.-year per ton of zinc. Loss in melting down the cathode zinc only 3 percent, kept so low by plunging the cathodes into molten zinc covered by a flux, while excluding air as far as possible.

The cost of the anodes has been decreased and their permanence increased by Dr. Max Huth. He makes anode plates of manganese peroxide, held in place by a carbon connector. Their life is one year, in continuous running.

Dr. Engelhardt finishes by stating that large experimental plants have been operated by Siemens & Halske in England and in America, and that a large commercial plant is projected.

The writer believes that the sulphate process with subsequent electrolysis with insoluble anodes may be misunderstood and misused. It is extremely difficult to deposit and win zinc from an acid solution, and the more acid it becomes and the smaller the amount of zinc it contains the greater the difficulty. If, therefore, the ore is roasted as far as possible to sulphate, and the zinc sulphate electrolyzed, the sulphur of the ore will be largely produced as dilute sulphuric acid, which must then be gotten rid of. It seems more logical to roast the sulphide ore largely to oxide than leach it with sulphuric acid and electrolyze this in two compartment cells with thin diaphragms, passing the zinc-bearing solution first through the cathode compartments, and afterwards through the anode compartments, and thus depositing the greater part of the zinc from solutions which have not become acid by electrolysis.

As regards the anodes, it appears that the electrolysis of copper sulphate is succeeding admirably in Chuquicamata, Chile, with fused magnetite (Fe_3O_4) anodes, which are stated to be absolutely permanent and unattacked. The magnetic iron oxide is melted in an electric furnace and cast into shape, iron conducting wires being embedded in it to act as connections. There appears to be no reason why such could not be used in the zinc sulphate electrolysis with equal success.

DISCUSSION.

CARL HERING: There is a method which Prof. Richards did not mention in his paper. If a spongy lead anode is used in a solution of sulphate of zinc, the zinc deposits on the cathode, while the SO_4 will be "deposited" on the lead plate (chemically combined with it) and will be retained by it; therefore the acid radical will be removed from the solution as fast as it is liberated, hence the solution will not accumulate acid, and one can get practically all of the zinc out of the solution. The spongy lead plate can then be immersed in another cell, and with a reverse current one can liberate the acid again as such. In this way I have easily obtained over 90 percent of the zinc out of the zinc sulphate solution at an ampere-hour efficiency of over 90 percent.

F. A. LIDBURY: In view of the generally accepted idea, as expressed in this paper, that zinc deposition can only be efficiently carried out with very slightly acid solutions and with a low current density, it is of extreme interest to observe the results of Pring and Tainton.[1] These authors find that with simultaneously increasing acidity and current density, particularly in presence of a small amount of collodial matter, the efficiency curve starts to rise, and in a solution containing 140 grams Zn and 125 grams H_2SO_4 per liter, efficiencies over 95 percent efficiency can be obtained with a current density of 40 amperes per square decimeter. The conditions under which such high figures can be obtained seem to be fairly narrow; for instance, the increase of collodial matter above a certain small amount leads to some deterioration; but, as the authors seem to have fallen into the sinful practice of varying more than one condition at once, it is not advisable to try to draw too many conclusions from their work, which deserves to be repeated and considerably extended.

CARL HERING: Mr. Lidbury's remarks recall a curious little experiment which I made many years ago. If zinc is deposited on a mercury cathode in the bottom of a beaker, the anode being considerably smaller in diameter, at rather high current densities the mercury will be found to gas very freely, but immediately

[1] Journal Chemical Society, London, **105**, 710 (March, 1914).

under the cathode there will be a sharply defined area which is absolutely free from gas. Something must be going on there; apparently it is the deposition of zinc without the evolution of hydrogen. I do not remember now what the current density was, but it was considerably higher than what is usually used in practice. I attempted at one time to get the whole area of the cathode free from that gas in that way, but did not follow up the test. The current density was high enough to heat the solution, so that it did not seem to me to be anything commercially practicable.

J. W. RICHARDS: The re-solution of the zinc would be proportional to the concentration of acid present. I have not read the article alluded to by Mr. Lidbury, but I should expect, other things being equal, that the higher the current density the greater the efficiency of zinc deposition would be, since the action of the acid would be constant for a given concentration, while the rate of deposition of zinc would vary directly with the current.

F. A. LIDBURY: A modification of that consideration will help to explain some of the results of Pring and Tainton. I was impressed by the connection between clean deposits and high efficiency in their results; where their deposits began to tree, get rough, and so on, the efficiency appears to fall off. In other words, while the rate of deposition is constant, the rate of re-solution increases with the roughening of the surface. It is quite clear, however, that in general their results show that, under the high current densities used, the more acid they have, up to a certain limit, the higher the efficiency.

J. W. RICHARDS: The concentration of zinc in solution being, of course, high?

F. A. LIDBURY: Yes.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

ADDITION AGENTS IN THE DEPOSITION OF ZINC FROM ZINC SULPHATE SOLUTION.

By O. P. Watts and A. C. Shape.

This paper presents the effect of the separate addition of over two score different organic substances to a zinc plating solution.

The electrolyte was made by adding an excess of zinc to dilute sulphuric acid. The solution had an acid reaction and contained 25 percent of $ZnSO_4.7H_2O$. The amount of organic substance added was one gram per liter. Except when otherwise stated, the solutions were electrolyzed for two hours at about 22° C., with a zinc anode and an iron cathode, at a current density of about 10 amperes per square foot (1.1 amperes per sq. dm.). For comparison, the well-known Meaker galvanizing solution was electrolyzed under similar conditions.

The majority of the substances added had an injurious rather than a beneficial effect upon the deposit. The most common defect was the production of vertical grooves or striations, shown in various degrees by cathodes 25, 13 and 32 of the photograph. Cathode 1, from the Meaker solution, is typical of the best deposits. Cathode 47, a 16-hour deposit with eikonogen as addition agent, shows the mossy tufts which frequently appear on zinc deposits. Cathode 48 shows the effect of amidol in the same time, and resembles a thickly-planted apple orchard.

The results, arranged in tabular form, follow:

No.	Addition Agent	Current Density Amperes		Deposit
		Per Sq.Dm.	Per Sq. Ft.	
1	Meaker solution.	1.23	11.2	Excellent, non-crystalline, adherent.
2	$ZnSO_4$—no add'n	1.20	10.9	Poor, striated.
3	Acetanilide	1.17	10.6	Very poor, badly striated.
4	Acetphenetidin .	1.26	11.5	Very poor, striated, dark.
5	Amidol	1.20	10.9	Poor, pitted.
6	Benzoic acid....	1.27	11.5	Good, non-crystalline, adherent.
7	Betanaphthol ...	1.27	11.5	Excellent.
8	Caffeine	1.20	10.9	Fair, crystalline.
9	Creosote	1.38	12.5	Fair, crystalline, slightly striated.
10	Dextrine	1.20	10.9	Poor, striated, granular.
11	Eikonogen	1.23	11.2	Very good, smooth, but dark.
12	Eucalyptol	1.20	10.9	Bad, striated, very dark.
13	Formin	1.20	10.9	Poor, striated.
14	Gallic acid	1.17	10.6	Very poor, striated.
15	Gelatine	1.32	12.0	Poor, crystalline, dark.
16	Glucose	1.17	10.6	Poor, striated.
17	Gum arabic	1.20	10.9	Fair, slightly striated.
18	Gum copal	1.27	11.5	Very poor, badly pitted.
19	Gum dammar ..	1,20	10.9	Very poor, striated, pitted, non-adh'nt.
20	Gum guaiac	1.14	10.4	Bad, striated, non-adherent.
21	Gum sandarac ..	1,20	10.9	Very poor, striated, pitted.
22	Gum tragacanth.	1.17	10.6	Very poor, striated, pitted, non-adh'nt.
23	Hydroquinone ..	1.23	11.2	Poor, striated, pitted.
24	Isinglass, Brazil.	1.27	11.5	Bad, striated, crystalline, dark.
25	Licorice	1.27	11.5	Very bad, striated, very dark.
26	Oil of cedar.....	1.23	11.2	Bad, striated, dark, non-adherent.
27	Oil of cloves....	1.27	11.5	Bad, striated, dark.
28	Oxalic acid	1.17	10.6	Poor, striated.
29	Peptone	1.23	11.2	Bad, dark, non-adherent.
30	Phenol	1.29	11.8	Fair, slightly striated and pitted.
31	Pyrocatechin ...	1.23	11.2	Very poor, striated.
32	Pyrogallol	1.23	11.2	Fair, slightly striated.
33	Salicin	1.20	10.9	Very poor, striated, pitted.
34	Salicylic acid....	1.27	11.5	Very poor, striated.
35	Salol	1.20	10.9	Very poor, badly striated.
36	Saponin	1.20	10.9	Very poor, striated.
37	Resorcine	1.13	10.3	Poor, striated, pitted.
38	Tannic acid	1.27	11.5	Very poor, gray, striated, granular,
39	Tartaric acid ...	1.20	10.9	Poor, striated. [pitted.
40	Terpin hydrate..	1.30	11.8	Fair, crystalline.
41	Turkey-red oil..	1.20	10.9	Poor, crystalline.
42	Turpentine	1.20	10.9	Bad, striated, non-adherent.

Addition agents which are insoluble in water were dissolved in alcohol before adding them to the electrolyte.

Those addition agents which gave the best results, *viz.*, gum arabic, benzoic acid, betanaphthol, caffeine, eikonogen, formin, pyrogallol and terpin hydrate, were tested repeatedly for different

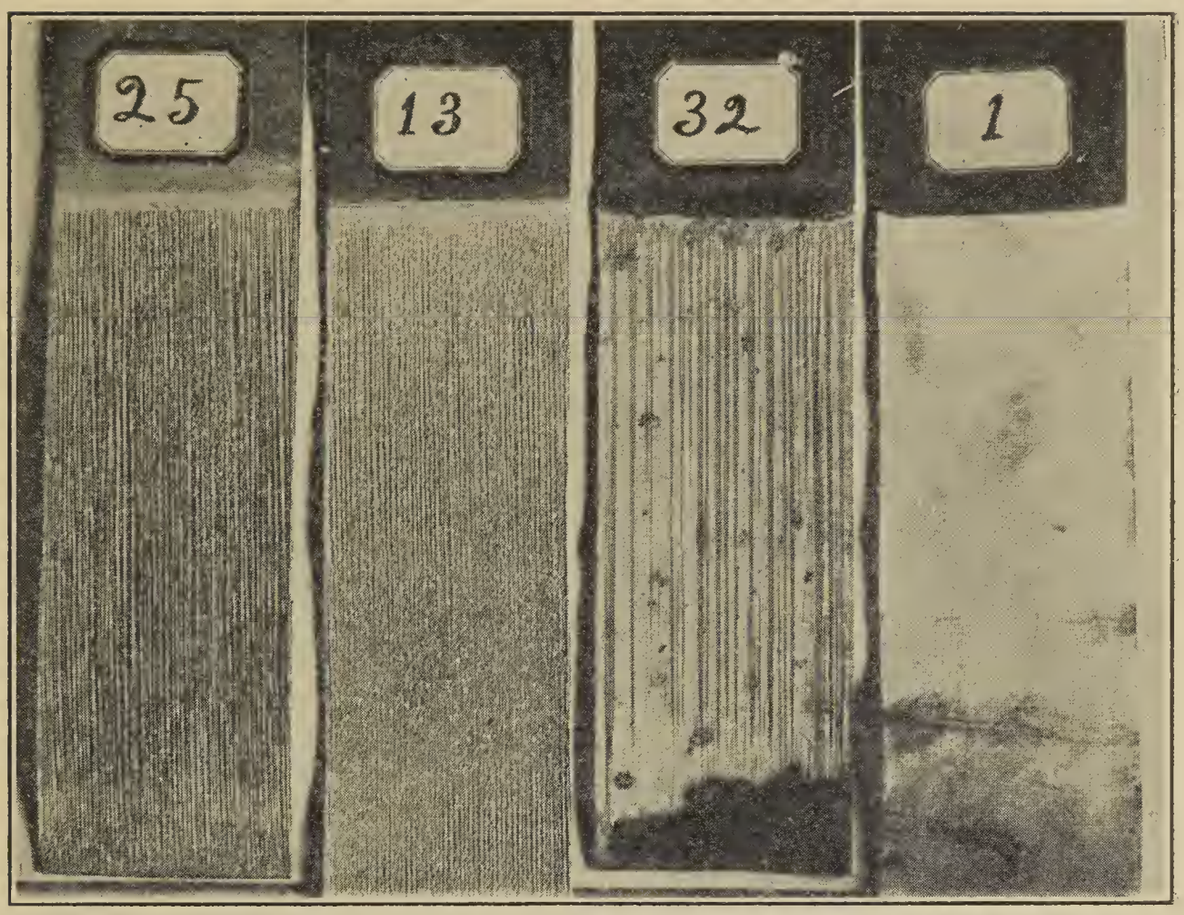


FIG. 1.

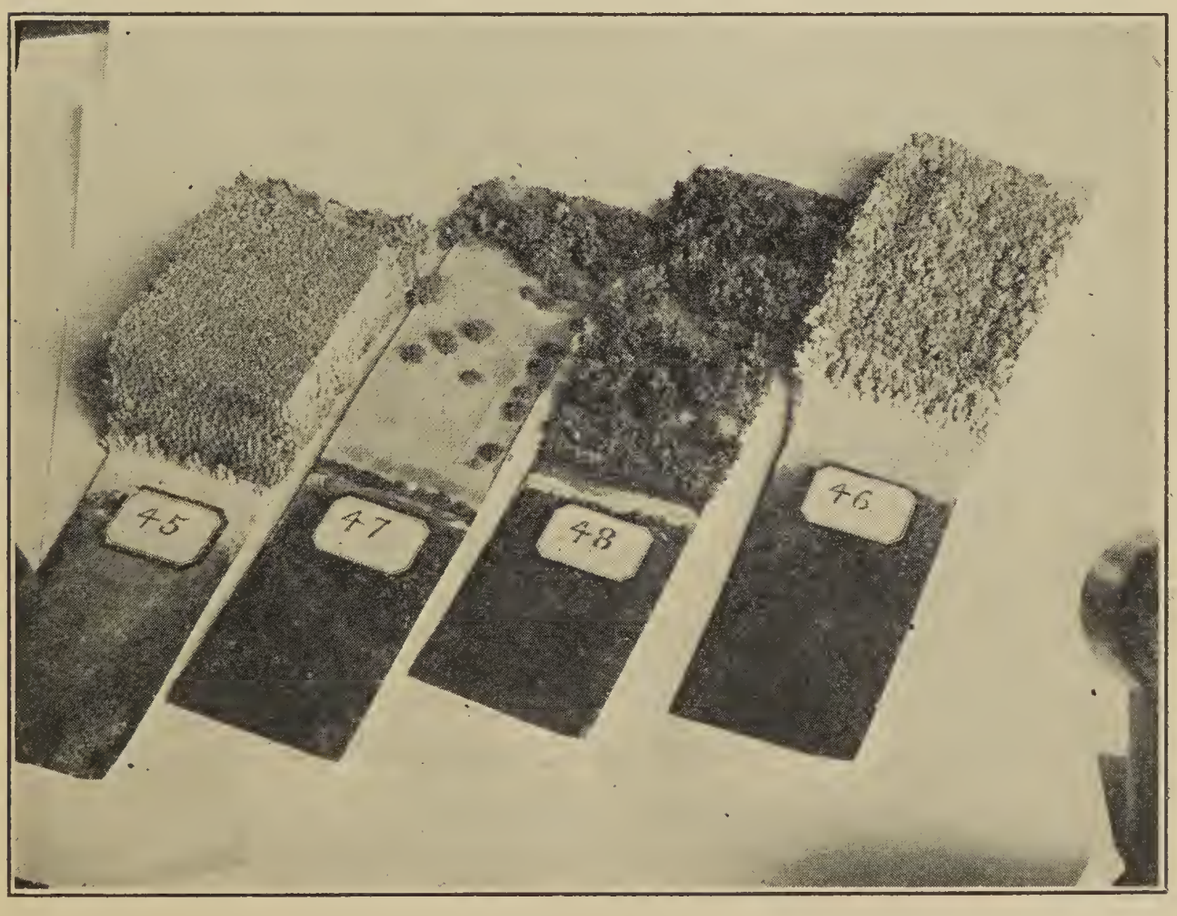


FIG. 2.

lengths of time. These tests resulted in the selection of betanaphthol, eikonogen and pyrogallol as the best addition agents.

Solutions containing these three reagents were electrolyzed for seven days at 0.5 ampere (10.5 amperes per square foot (1.16 amperes per sq. dm.)) in series with the Meaker solution. Although most experimenters have reported that addition agents are used up during electrolysis, and so require replenishing from time to time, it is claimed that the Meaker solution is self-sustaining and requires no additions to it during use.

After a number of hours' electrolysis of the above solutions, all except the betanaphthol became rough and unsatisfactory. It was only after several days that this deposit also became rough and spongy. Cathode 45 is the 7-day deposit from the Meaker solution, and cathode 46 that from the betanaphthol solution.

Whether or not failure of the electrolytes was due to exhaustion of the addition agents, and can be prevented by adding a fresh supply of these from time to time, was not determined in these experiments. There is, of course, also the possibility that some of the addition agents which failed under the conditions described may prove effective at a higher temperature or with some other zinc salt than the sulphate as electrolyte.

Although these experiments constitute but a preliminary and hasty survey, they have resulted in the finding of three promising addition agents for the deposition of zinc from a solution of zinc sulphate, *viz.*, eikonogen, pyrogallol and betanaphthol. The latter is best, and, so far as the writers have observed, has not heretofore been suggested as an addition agent for the deposition of any metal.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

J. N. Pring (*Communicated*): An investigation extending over some years, which has been carried out by Mr. U. C. Tainton and myself,[1] on the influence of colloids on the electrodeposition

[1] C. f. Brit. Pat. 7235 of 1911. U. S. Pat. 1,059,233. Trans. Chem. Soc. London, **105**, 710 (1914).

of zinc, has shown that deposits similar to those reproduced in the paper of Messrs. Watts and Shape can be obtained under the following conditions: An electrolyte is taken of zinc sulphate together with from 10 to 20 grams of free sulphuric acid per 100 cc., and a small quantity of a colloid such as gum arabic. A current density at the cathode of between 20 and 50 amp. per square dcm. is employed. When using lead anodes, this current can be obtained with 4.5 to 5.0 volts in the above electrolyte. The current efficiency varies from 90 to 96 percent. With these conditions, considerable quantities of most impurities have no great deleterious effect on the deposition of the zinc. Moreover, iron, which is the most troublesome impurity in ordinary practice, remains for the most part in the electrolyte during electrolysis, on account of passivity or retardation phenomena. These conditions have been found to be the most favorable for conducting the extraction of zinc from solutions made from ores and for the purpose of electro-galvanizing, as deposits of very high luster are obtained with suitable colloids.

It would be of great interest if Messrs. Watts and Shape mentioned the current efficiency obtained in their electrolyses and also if measurements have been made with commercial solutions.

O. P. Watts: Unfortunately, no determinations of current efficiency were made in our experiments, but the absence of noticeable evolution of gas at the cathode would indicate an efficiency of 95 percent or above.

I wish to congratulate Dr. Pring on two notable achievements: The deposition of zinc on stationary cathodes at 465 amperes per square foot, smooth and solid enough for galvanizing, and the attainment of current efficiencies of 90 to 95 percent from solutions containing 20 percent of free sulphuric acid, a degree of acidity which even copper refiners do not venture to use. Dr. Pring's experiments disclose new and undreamed-of possibilities in the electrometallurgy of zinc, and emphasize the importance of trying experiments which, in the light of our present imperfect knowledge of the laws of nature and the properties of matter, would seem sure to fail.

H. E. Holbrook,[2] using faintly acid zinc solutions, probably

[2] B. S. Thesis, University of Wisconsin, 1912.

richer in iron than Dr. Pring's, found the same tendency for the iron to stay in solution. At 13 amperes per square foot, with stationary cathodes and soluble anodes, he electrolyzed for 30 minutes a solution containing 20 grams of zinc sulphate and 50 grams of ferrous sulphate per liter, and obtained a deposit containing 6.21 percent of iron. In a similar experiment the electrolyte contained 30 grams of each sulphate per liter, and the deposit was only 1.25 percent iron. Whatever may be the cause of this unexpected phenomenon, I do not see how passivity can explain the failure of the iron to plate out, once it has dissolved in the electrolyte.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

ELECTRODEPOSITION OF CADMIUM

PART I.—REVIEW

By Frank C. Mathers and Hugh M. Marble.

This review of the literature of the electrodeposition of cadmium was preliminary to a series of experiments upon the electrodeposition of cadmium from some hitherto untried solutions. It has been made as complete as our library facilities have permitted. The composition of the baths, the current density, voltage, the appearance of the cathode and especially the effect of the conditions and composition of the bath upon the deposit have been considered the important things.

The review has been subdivided as follows:

I. CADMIUM SALTS OF INORGANIC ACIDS.

- *(a) Sulphate solutions.*
- *(b) Nitrate solutions.*
- *(c) Halide solutions.*
- *(d) Fluosilicate solutions.*
- *(e) Cyanide solutions.*
- *(f) Phosphate solutions.*

II. AMMONIACAL SOLUTIONS.

III. CADMIUM SALTS OF ORGANIC ACIDS.

- *(a) Oxalate solutions.*
- *(b) Acetate, formate, lactate and succinate solutions.*
- *(c) Tartrate solutions.*

IV. COMMERCIAL PLATING AND REFINING.

This outline could not be rigidly followed without some repetition. Generally, all the experiments in one article have been placed under the heading of the solution which gave the best

results. Unless otherwise stated, all the "amperes" mean "amperes per 100 sq. cm. at the cathode," and all volumes are 100 cc. Most of the experiments which have been done upon the deposition of cadmium were for quantitative determinations. In all cases where good deposits were obtained there seems to have been no difficulty in washing the cathodes with water and alcohol and in drying without oxidation before weighing.

I. CADMIUM SALTS OF INORGANIC ACIDS.

(a) Sulphate solutions.

Wrightson[1] found, by qualitative electrolysis of a solution of cadmium sulphate, that cadmium was poorly adapted to a quantitative determination by electrolysis. Metallic cadmium was deposited easily and quickly from an acid solution, but not in compact, weighable condition. The feathery, hanging scales on the edges of the cathode produced, in a short time, short-circuits.

Luckow[2] says that cadmium is precipitated completely in a metallic form of a zinc gray color from dilute neutral solutions of the sulphate, nitrate or acetate. The amount of free acid in the sulphate solution may reach 1.5 to 2 percent before the separation of cadmium is hindered. Cadmium also precipitates completely from solutions to which an excess of sodium or ammonium acetate has been added.

Smith[3] concluded that cadmium sulphate was best for quantitative work. The chloride or nitrate with the addition of sodium acetate also gave good results. The presence of free sulphuric acid caused by the breaking up of the cadmium sulphate is not injurious, consequently it is not necessary to add the sodium acetate. Cadmium was separated from copper by electrolysis of a solution acidified with nitric acid. The cadmium remaining in solution was deposited after the nitric acid had been removed by evaporation with sulphuric acid.

Wieland[4] deposited cadmium from weak sulphuric acid solution.

Smith and Frankel[5] found that cadmium was not deposited

[1] Z. anal. Chem., **15**, 303 (1876).
[2] Z. anal. Chem., **19**, 16 (1880).
[3] Am. Chem. J., **2**, 42 (1880).
[4] Ber., **17**, 1611 (1884).
[5] Am. Chem. J., **11**, 352 (1889) and **12**, 110 (1890).

from a solution containing 10 cc. of sulphuric acid (1.09 sp. gr.) with a current of 0.03 amp. This gave a method of separating copper from cadmium.

Kollock[6] used a solution of cadmium sulphate containing 0.16 gm. of the metal, 3 cc. sulphuric acid (1.09 sp. gr.) and 125 cc. water. A current of 0.078 amp. and a voltage of 2.61 were used. The temperature was 65°. The deposition was complete in 5 hours. The deposits weighed 0.5 mg. more than theory.

Balcahowsky[7] added to the solution of 2 gms. of cadmium in 150 cc. of water, 3 gms. of urea, 6 cc. of formaldehyde, or 6 cc. of acetaldehyde. This solution was electrolyzed at 40°–60° for 8–10 hours with 0.3–0.6 amp. and 2.5–3.3 volts. Bright deposits were obtained.

Medway[8] used a rotating platinum dish as cathode. He deposited 0.2 gm. of cadmium from a solution slightly acid with sulphuric acid in 10–15 minutes. The current was 5–6.6 amp., and the cathode rotated 650–700 times per minute. Ammonia was gradually added near the end of the experiment to prevent solution of the deposited cadmium by the free acid.

Exner[9] deposited cadmium using an anode rotating 600 times per minute. With 0.27 gm. of cadmium as sulphate, 3 cc. of sulphuric acid (1:10), 110–125 cc. of solution and 5 amperes, the deposit of cadmium was crystalline and loose but sufficiently adherent to weigh. With only 1 cc. of sulphuric acid the deposits were "beautifully crystalline and very satisfactory." With 0.55 gm. cadmium, 2 gm. sodium acetate and 0.5 gm. potassium sulphate (to increase the conductivity) quantitative deposits were obtained. With 0.55 gm. cadmium, 5 gm. sodium hydroxide, and 2 gm. potassium cyanide, the deposits were "white, compact and very satisfactory." Deposition was complete in 10–15 minutes.

Carhart[10] prepared cadmium amalgam for use in standard cells by deposition from a saturated solution of pure cadmium sulphate using pure mercury as cathode and sticks or a button of the pure cadmium of commerce as anode. The voltage was kept below 0.3. A crystallizing dish held the mercury cathode,

[6] J. Am. Chem. Soc., **21**, 925 (1899).
[7] Compt. rend., **131**, 384 (1900).
[8] Am. J. Sci., (4) **18**, 56 (1904).
[9] J. Am. Chem. Soc., **25**, 903 (1903).
[10] Trans. Amer. Electrochem. Soc., **6**, 120 (1904).

and a second crystallizing dish held the anode or was placed below the anode to catch the slime. This method gave an amalgam free from zinc and oxides or dross.

Ashbrook[11] used a rotating anode for the deposition and separation of cadmium from a number of other metals. The electrolyte contained 1 cc. of conc. sulphuric acid and 0.27 gm. of cadmium in 125 cc. Five amperes and 5 volts were used for 10 minutes. From chromium (0.25 gm.) the cadmium was separated as "beautiful, white, crystalline," and from aluminum (0.25 gm.) as "excellent, although slightly spongy, but perfectly adherent." The deposition was incomplete in the presence of chromium.

Davison[12] deposited cadmium, using a rotating cathode. The electrolyte contained 0.2–0.5 gm. cadmium and 0.5–1 cc. sulphuric acid (1:10). Three to four amperes at 0.3–14 volts were used. The anode rotated 430–940 times per minute. The solution was heated before each determination until bubbles showed upon the bottom of the dish. Gray, well-adhering deposits were obtained. A small amount of free acid was advantageous.

Flora,[14] using a rotating anode, determined cadmium in a solution containing 0.2–0.25 gm. of the metal and 10–15 drops of sulphuric acid (1:4) in 50 cc. of water. Complete deposition was obtained in 15 minutes. At the end of the electrolysis the sulphuric acid was neutralized with ammonium hydroxide to prevent the solution of the metal. Six to nine amperes were used. Deposition was also tried from solutions of cadmium sulphate to which 3 gm. urea, 2 cc. of formalin or 2 cc. of acetaldehyde had been added. The rate of deposition was slow, due to the resistance of the solution. Eleven and eight-tenths volts gave only 0.1–0.8 amp. "The deposits were gray, compact and quickly dried." The addition of potassium sulphate to increase the conductivity produced spongy deposits. The addition of 5–10 drops of sulphuric acid gave better deposition.

Sherwood and Allemann[15] experimented with the use of tin cathodes in the quantitative deposition of cadmium. They used anodes rotating 500–700 times per minute, and cast or spun tin

[11] J. Am. Chem. Soc., **26**, 1288 (1904).
[12] J. Am. Chem. Soc., **27**, 1275 (1905).
[14] Am. J. Sci., (4) **20**, 270 (1905); Z. anorg. Chem., **47**, 1.
[15] J. Am. Chem. Soc., **29**, 1065 (1907).

dishes as cathodes. The electrolyte was the same as that employed by Exner.

Holmes[16] used a rotating dish as anode, and a large platinum dish of 200 cc. capacity as cathode. A current of 1 ampere, which is much below that usually employed, was used. Currents below 0.3–0.4 ampere were not useful. Cadmium was best deposited from a solution containing 1 cc. sulphuric acid (1.09 sp. gr.) with a current of 0.3–0.4 amp. in 45 minutes. Ammonium acetate and acetic acid electrolytes were also used. Excellent separations could be obtained from zinc, magnesium, manganese and nickel with the low current densities. With higher current densities, such as those used by Ashbrook and by Davison, some of the zinc and nickel were deposited with the cadmium.

Stoddard[17] used a mercury cathode weighing 40 gms. in a beaker of 45–50 cc. The anode was a flat platinum wire 0.5–1 cm. from the surface of the mercury. The electrolyte contained 0.27 gm. cadmium as nitrate, 5–6 drops of sulphuric acid and 25 cc. of water. A current of 5–7 amp. for 10 minutes completely deposited the cadmium. With stationary platinum gauze electrodes of special shape, satisfactory depositions were made in 5 minutes. In both cases the stirring of the solution was brought about by the gases and the heat produced by the heavy currents.

Benner[18] agitated or stirred the solution by the gases evolved and by the heat produced by the current. Much higher currents than those usually employed may be used. A current of 10 amp. was used with the gauze electrodes, and 35–40 amp. with the mercury cathode. The rapid deposition in a weighable form was due, at least in part, to this method of stirring. Fifty-seven hundredths gm. of cadmium was deposited in 10 minutes from 20 cc. of a solution containing 5 drops of conc. sulphuric acid. Four amperes were used. Four drops of nitric acid could be substituted for the sulphuric acid. It did not seem to make much difference whether the solution was hot or cold.

Hulett and Perdue[19] and Laird and Hulett[20] have determined the atomic weight and the electrochemical equivalent of cadmium

[16] J. Am. Chem. Soc., **30**, 1865 (1908).
[17] J. Am. Chem. Soc., **31**, 385 (1909).
[18] J. Am. Chem. Soc., **32**, 1231 (1910).
[19] J. Phys. Chem., **15**, 147.
[20] Trans. Am. Electrochem. Soc., **22**, 385 (1912).

by deposition from a sulphate solution. Mercury in an amalgamated platinum crucible was used as cathode. The great advantage of such a cathode is that no liquid can get between the mercury and the container. Very great accuracy was claimed for the work. The mercury surface was perfectly bright at the end of the electrolysis. Since mercury is volatile from a mercury cathode if the electrolyte becomes heated, a low temperature was maintained by packing the apparatus in ice.

Breyer[21] claims that the most accurate method for the determination of small amounts of cadmium is by electrical precipitation. Cadmium can be deposited from solutions containing up to 10 percent of sulphuric acid. Accuracy within 0.2 percent may be attained.

(b) Nitrate solutions.

No description of the nature of the cadmium deposited from a nitrate solution containing nitric acid was found. Nitric acid solutions were used in the separation of cadmium from other metals, in which cases the cadmium remained in solution.[22, 23, 24, 3, 75]

Stoddard[17] deposited the cadmium as an amalgam from a nitric acid solution.

Balachowsky[25] obtained clean, crystalline, adherent deposits of cadmium from a solution containing 1 gm. cadmium sulphate, 5 cc. of nitric acid for each gm. of salt and 150 cc. water. The solution was electrolyzed at 60° by a current of 0.4 amp. at the beginning and 0.6 amp. at the end.

Flora[26] found that cadmium could not be deposited in a satisfactory condition from nitrate solutions except after neutralization with sodium hydroxide and addition of potassium cyanide.

Benner[18] said that nitric acid could be substituted for sulphuric acid in his method, using a gauze or a mercury cathode.

(c) Halide solutions.

Bertrand[27] employed such a low voltage (from a thermopile) that these solutions of cadmium chloride, bromide and iodide

[21] 8th Int. Cong. App. Chem., **27**, 26 (1912).
[22] Classen and Ludwig, Ber., **14**, 323 (1886).
[23] Rudorff, Z. angew. Chem., **7**, 388 (1894).
[24] Smith, Electrochemical Analysis.
[25] Comp. rend., **131**, 384 (1900).
[26] Am. J. Sci., (4) **20**, 270 (1905).
[27] Comp. rend., **83**, 855 (1876).

were not appreciably decomposed except after the addition of a few drops of sulphuric acid in each case. Cadmium chloride gave a poorly adherent deposit. Cadmium-ammonium chloride gave a zinc gray, not very adherent, deposit. Cadmium bromide gave a white, very adherent deposit which could be beautifully polished. Finally, long, brilliant needles were produced in this solution. Cadmium-ammonium bromide gave a white adherent deposit. Cadmium-ammonium iodide gave a spongy deposit. The bromide or sulphate solution, of course acidified with a few drops of sulphuric acid, was considered the best for obtaining a deposit of cadmium. Cadmium sulphate with a few drops of sulphuric acid was found to give a poorly adherent deposit.

Classen[28] deposited cadmium from a solution weakly acid with sulphuric acid to which 15 percent of ammonium chloride had been added. Fifteen gm. of cadmium was deposited in 10–15 hours with a current of 0.07–0.09 amp.

Some authors consider that the addition of ammonium chloride to cyanide baths produces better deposits,[37] while other writers[42] claim that no salts except the cyanides should be present.

Patten and Mott[29] obtained smooth deposits of cadmium from a saturated solution of cadmium chloride in acetone, using 0.1 amp. and 1.5 volts.

(d) Fluosilicate solutions.

Senn[30] deposited cadmium from a fluosilicate bath. He reasoned that, since non-crystalline lead could be deposited from a fluosilicate bath containing glue, other metals could be deposited in a smooth condition also. Attempts to obtain thick deposits of cadmium from ordinary electrolytes containing sulphuric acid gave trees which soon produced short-circuits. Three hundred cc. of 20 percent hydrofluosilicic acid, 10 gms. of crystallized cadmium sulphate and 0.1 gm. glue were electrolyzed for 18 hours with a current of 0.59 amp. The cathode was crystalline but irregular. There was a tendency to form solitary or isolated crystals. In another experiment where the gelatine was increased to 0.2 gm., and the current to 1.07 amp., the deposit was very

[28] Ber., **17**, 2470 (1884).
[29] Trans. Am. Electrochem. Soc., **15**, 529 (1909).
[30] Z. Electrochem., **11**, 236 (1905).

compact and adherent. The surface was rough, but the increased quantity of gelatine seemed to prevent the formation of growths. In a third experiment, where 0.3 gm. of gelatine and 1.07 amp. were used, the deposit showed smaller projections. The plate was so dense and firm that it could be bent gently without breaking. Hydrogen was deposited during the early experiments, consequently the percentage of cadmium in the bath increased from 1.23 to 2.59 percent.

(e) Cyanide solutions.

Beilstein and Jawein[31] dissolved cadmium sulphide, oxide or carbonate in nitric or hydrochloric acid, neutralized with sodium hydroxide, and added potassium cyanide until the precipitate was just redissolved. The metal deposited in a more compact form from the nitrate than from the chloride solution. The deposit was granular if the solution was too concentrated or if the current was too large. With two Bunsen cells the deposit was a beautiful bright gray, without black spots. Two-tenths gm. of cadmium was contained in 75 cc. of solution.

Smith and Frankel[32] found that cadmium was deposited more readily than zinc, cobalt and nickel from cyanide solutions. If the potassium cyanide was not in excess, some zinc was deposited with the cadmium even with the weak current. About 0.2 gm. of cadmium was separated from the other metals in 18–20 hours with a current of 0.027 amp. The solution contained 4.5 gm. potassium cyanide in 200 cc.

Hintz[33] reviewed the methods of depositing cadmium.

Lorimer and Smith[34] determined the atomic weight of cadmium by the electrolysis of pure cadmium oxide dissolved in potassium cyanide. The current from 10 copper sulphate gravity cells was used. The maximum and minimum values were 112.182 and 111.908.

Rudorff[35] says that deposits from solutions containing sodium acetate and acetic acid, oxalates, ammonia, or sodium pyrophosphate and ammonia did not give closely agreeing results.

[31] Ber., **12**, 759 (1879).
[32] Am. Chem. J., **11**, 352 (1889), and **12**, 104 (1890).
[33] Z. anal. Chem., **29**, 680 (1890).
[34] Z. anorg. Chem., **1**, 364 (1892).
[35] Z. angew. Chem., **6**, 35 (1892).

Cadmium deposited as a dull gray cohesive metal from cyanide solutions. Enough cyanide was added to the neutral solution to redissolve the precipitate which formed first.

Smith[36] separated silver from cadmium, using 0.05 gm. of each in a solution containing 1.5 gm. of potassium cyanide. A current of 0.4 amp. was passed through the solution, heated to 65°. The silver, free from cadmium, was completely deposited in 3.5 hours.

Rimbach[37] explained the advantages of the cyanide method. This method does not require much attention; a considerable mass of the metal may be deposited, and the conditions are simple. The only disadvantage is that the time of electrolysis is somewhat longer than usual. About 3 gm. of 98 percent potassium cyanide was added to the neutral solution of cadmium sulphate or chloride. The solution was diluted to 150–200 cc. and electrolyzed at ordinary temperature with 0.02–0.04 amp. over night or for 12–16 hours. The metal deposits were silver white in color. The results seemed to be better using some ammonium chloride in the solution. The solution was colored yellow or brown at the end if a strong enough current had been used. Too strong a current made the metal black and granular. Cadmium and copper were separated from a solution containing 5 gm. of potassium cyanide with a current of 0.02–0.04 amp.

Neumann[38] states that only about 0.08–0.09 gm. of cadmium can be deposited per hour in a good condition from a cyanide bath. While this rate is low, the total quantity that can be deposited is greater than that for other solutions where the limit is about 0.15 gm.

Hardin[39] determined the electrochemical equivalent of cadmium by electrolyzing, in series, solutions of potassium-silver cyanide and potassium-cadmium cyanide. Platinum wires were used as anodes, and platinum dishes as cathodes. The results were not concordant. The solutions were made by dissolving cadmium chloride and cadmium bromide in potassium cyanide.

Stortenbecher[40] separated cadmium from iron. Two to three

[36] J. Am. Chem. Soc., **16**, 1894 (1894).
[37] Z. anal. Chem., **37**, 384 (1898).
[38] Z. Electrochem., **2**, 231 (1896).
[39] J. Am. Chem. Soc., **18**, 1016 (1896).
[40] Z. Electrochem., **4**, 409 (1898).

gm. of potassium cyanide was added to the solution acidified with a few drops of sulphuric acid. The solution thus formed was heated until clear and then diluted to 200–250 cc. If much ferric salt was present, the weakly acid solution was reduced with sodium sulphite. Ferric salts caused a separation of ferric hydroxide upon the cathode. However, it did not adhere, consequently the cadmium deposit was entirely free from iron.

Kollock[41] reinvestigated and determined the best conditions for the determination of cadmium from a cyanide solution. One gram of potassium cyanide was used for a solution containing 0.16 gm. of cadmium as sulphate. This solution was heated to 60° and electrolyzed with 0.04–0.06 amp. and 2.9 volts. Using 2 gm. potassium cyanide, 0.02 amp. and 2 volts, in a hot solution, silver and mercury may be completely deposited from cadmium. Four to seven hours were required for the deposition.

Miller and Page[42] electrolyzed 0.2 gm. cadmium as chloride in 150 cc. water with just enough potassium cyanide to redissolve the precipitate. One-tenth to sixteen-hundredths amp. was used for 16 hours. An excess of potassium cyanide or the presence of strange salts was not good. When the cadmium sulphide was dissolved in hydrochloric acid, the excess of acid was evaporated off and not merely neutralized. Accuracy was about 0.2 mg.

Davison[44] used a solution containing 1 gm. sodium hydroxide, 3–4 gm. potassium cyanide with an anode rotating 580 times per minute. The addition of the sodium hydroxide prevented the solution from creeping over the edges of the electrolyzing dish. With large amounts of sodium hydroxide "the deposits had a cloudy gray appearance," but with the minimum amount (about 1 gm.) the deposit was "lustrous and of a beautiful silver-white color." There was a loss of 4 mg. from both the platinum anode and cathode during twenty determinations.

Stoddard[17] also rapidly deposited cadmium with stationary electrodes from solutions containing just enough potassium cyanide to redissolve the precipitate.

Price and Humphreys[45] used a rotating cathode in a solution containing 1.5 gm. sodium hydroxide and 0.5 gm. potassium

[41] J. Am. Chem. Soc., **21**, 911 (1899).
[42] Z. anorg. Chem., **28**, 233 (1901).
[44] J. Am. Chem. Soc., **27**, 1275 (1905).
[45] J. Soc. Chem. Ind., **29**, 307 (1910).

cyanide in 10 cc. of water. Electrolysis was with 2 amp. for 30 min. in the cold. A good quantitative deposit was secured. A 5 amp. current also gave good results. Forty-nine hundredths gm. of cadmium could not be completely deposited in 15 minutes. They were unable to deposit the cadmium completely upon stationary electrodes by the method of Stoddard in the given time. Electrolysis for a longer time produced good results. They conclude that stationary electrodes are less suitable for rapid analysis than rotating electrodes. On the other hand, Ford[46] approved of the Stoddard method.

Benner and Ross,[47] experimenting with stationary gauze electrodes for the rapid deposition of cadmium, found that a good, uniformly bright deposit could be obtained only from cyanide solutions, although many other solutions were tried. Different concentrations of the solution gave good results. He used from 5 gm. of potassium cyanide to just enough for solution of the precipitate, and from 1 gm. of potassium hydroxide to just a faint alkalinity. The presence of the alkali prevents the formation of a yellow color from the decomposition of the cyanide during electrolysis. A discolored solution is likely to give high results. Three to four amp. at 5–11 volts were used for 60–75 minutes. Occasionally a deposit examined under the microscope showed a tendency to sponginess, but good quantitative results were always obtained. Variation in the concentration of the cyanide had much less effect than in the case of the silver deposition.

(f) Phosphate solutions.

Moore[48] did a little preliminary work upon the electrolysis of phosphate solutions. Cadmium was deposited from a metaphosphoric acid solution by a small current, while zinc remained in solution.

Brand[49] electrolyzed the double sodium pyrophosphate, which was brought into solution by 1 percent of sulphuric or phosphoric acid. With a current of 0.02–0.045 amp. the metal deposited in a bluish-white form, but showed indications of becoming spongy.

[46] Met. Chem. Eng., **8**, 229 (1910).
[47] J. Am. Chem. Soc., **33**, 1106 (1911).
[48] Chem. News, **53**, 209 (1886).
[49] Z. anal. Chem., **28**, 581 (1889).

The solution in glacial phosphoric acid gave better results. A solution of the phosphate in nitric acid could be used. With 1–2 percent of sulphuric acid and a current of 0.018–0.09 amp. the deposit was white, adherent and plainly crystalline. With a current of 0.9 amp., at the end, the deposition was complete. With more than 1 percent of sulphuric acid only the sulphate and not the phosphate was electrolyzed.

Smith[50] found that cadmium deposited easily from solutions of cadmium phosphate in free phosphoric acid. One-tenth gm. of cadmium as phosphate was precipitated by an excess of sodium phosphate (1.035 sp. gr.), and then was redissolved by 1.5 cc. phosphoric acid (1.347 sp. gr.). The deposit with 0.05 amp. showed a slight sponginess. The quantitative results were a little higher than theory. Since cadmium does not deposit readily from acid solutions, the current was increased near the end in order to obtain complete precipitation. Cadmium was separated from nickel, iron, zinc, aluminum and manganese in an electrolyte containing 20–40 cc. of di-sodium-phosphate and 2–3 cc. of phosphoric acid. A current of 0.03 amp. for 12 hours was used. The deposits were crystalline except for some slightly spongy spots.

Hintz and Weber[51] gave a very complete review of Smith's work.

Smith and Wallace[52] used about the same conditions as those above, except that the electrolyte was heated to 50°. The current was increased from 0.06 to 0.35 amp. after 4 hours. The results were good.

Flora[53] with a rotating cathode tried the solutions of pyrophosphates and phosphates as recommended by Brand and by Smith. Only fairly good results were obtained. Too large a current (above 1.5 and 3 amp., respectively) gave spongy deposits.

II. AMMONIACAL SOLUTIONS.

Clarke[54] found that cadmium could be completely precipitated by electrolysis from an ammoniacal solution, but that it came

[50] Am. Chem. J., **12**, 329 (1890) and **13**, 206 (1891).
[51] Z. anal. Chem., **31**, 201 (1892).
[52] J. Am. Chem. Soc., **19**, 870 (1897) and **20**, 279 (1898).
[53] Am. J. Sci., (4) **20**, 270 (1905).
[54] Ber. **11**, 1409 (1879); Am. J. Sci., (3) **16**, 200 (1878).

down as a spongy, porous mass containing various impurities which could not be washed out. Therefore the results were much too high.

Yver[55] advised against an ammoniacal cadmium sulphate solution.

Smee[56] found that the solution made by adding ammonia to cadmium sulphate until the precipitate just redissolved readily yielded a good deposit, while the simple solutions of cadmium sulphate or chloride were difficult to work.

Brand[49] found that the solution of cadmium pyrophosphate in ammonia was well adapted for quantitative work. An abundant addition of ammonia was required to prevent the formation of a white precipitate during the electrolysis. A current of 0.027–0.09 amp. was used. The deposit was thick, silver-white and smooth to the touch, but crystalline. With a higher current, branchy crystals were formed.

Davison[57] used a rotating anode. Cadmium hydroxide was precipitated by an excess of ammonium hydroxide. Sulphuric acid, which was then neutralized with ammonium hydroxide, was added to increase the conductivity. A current of 5 amp. gave gray, somewhat spongy deposits which could, however, be weighed. The liquid was always alkaline at the end of the deposition. The time of electrolysis could not be shortened by an increase in the quantity of ammonium hydroxide or by increasing the current. An ammoniacal acetate solution is inferior to a solution slightly acid with acetic acid.

III. CADMIUM SALTS OF ORGANIC ACIDS.

(a) Oxalate solutions.

The deposits which Classen and Reis[58] obtained from ammonium cadmium oxalate solutions were gray and adhered poorly, but gave quantitative results if only small quantities of cadmium were used.

Classen[59] described the advantages of electrolytes containing double ammonium oxalates.

[55] Bull. Soc. chim., **34**, 18.
[56] Macmillan, Electrometallurgy, 258 (1901).
[57] J. Am. Chem. Soc., **27**, 1275 (1905).
[58] Ber., **14**, 1622 (1881).
[59] Ber., **15**, 1096 (1882); D. R. P., 17,864, of 1881.

Wieland[60] deposited cadmium from an oxalate solution, using a current of 0.4 amp. The deposit was spongy and oxidized easily during drying.

Classen[61] says that cadmium can be deposited quickly in a bright, thick condition by electrolysis of a hot solution of the double oxalate salt which is kept acid during electrolysis by the addition of a cold saturated solution of oxalic acid. A current of 0.5–1.5 amp. was used. As soon as the current was started several cc. of oxalic acid were added and the solution was maintained weakly acid during electrolysis. Three-tenths to four-tenths gm. cadmium sulphate and 10 gm. of ammonium oxalate in 120 cc. of solution were used. The deposits were glistening bright.

Vortmann[62] found that cadmium can be deposited upon a platinum foil in a smooth, adherent condition only if very small amounts of the metal are present. Cadmium can be readily separated from the double ammonium oxalate salt as well as from an ammoniacal solution in the form of an amalgam. Four parts of mercury should be present for each part of cadmium. If too little mercury is used the amalgam separates in a crystalline form and does not cling well to the platinum electrode; consequently it is difficult to wash without loss. If the amalgam contains 4–6 parts of mercury for each part of cadmium it is so hard that it can be rubbed with the finger without loss. Eight parts of mercury to one part of cadmium gives a liquid amalgam which does not oxidize in the air and which can be weighed again after several days without any change in weight. Five grams of ammonium oxalate was added to the solution of cadmium and mercuric chlorides. This mixture was stirred in the cold until solution was complete. In a hot solution mercurous chloride may be precipitated. If more than 0.3 gm. of cadmium was present, a strongly ammoniacal solution containing 3 gm. of tartaric acid was used.

Eliasberg[63] obtained excellent results in the separation of cadmium and zinc by using 8–10 gm. potassium oxalate and 2–3 gm. ammonium oxalate. The solution was heated nearly to

[60] Ber., **17**, 1611 (1884).
[61] Ber., **27**, 2060 (1894).
[62] Ber., **24**, 2749 (1891).
[63] Z. anal. Chem., **24**, 548 (1886) and Inaugural-Dissertation, Heidelberg, 1895.

boiling and electrolyzed with 0.1–0.15 amp. for 6–7 hours. The cadmium deposit was crystalline, with a glistening surface.

Flora[64] with a rotating cathode always obtained a spongy deposit from ammonium oxalate solutions. Sodium oxalate, even when present in the smallest quantity necessary to give complete solution, gave results much too high.

(b) Acetate, formate, lactate and succinate solutions.

Smith[65] dissolved 0.14 gm. cadmium oxide in acetic acid and evaporated off the excess of acid upon the water bath. The metal deposited completely in 3 hours with two Bunsen cells. The deposit was in regular crystalline plates without sponge.

Luckow[66] said that cadmium could be completely deposited from solutions to which an excess of ammonium or sodium acetate had been added.

Yver[55] electrolyzed a warm solution of cadmium and zinc acetate or sulphate to which 2–3 gm. sodium acetate and a few drops of acetic acid had been added. Two Daniell cells were used. The cadmium deposited in a coherent crystalline coat. The zinc remained in solution. The time of electrolysis was about 3–4 hours for 0.2 gm. of each of the metals.

Heidenreich[67] found that the conditions given by Smith did not give satisfactory results either in reference to the quality or the quantity of the deposit. With a solution containing 1 cc. of 50 percent acetic acid in 120 cc. of solution, and a current of 0.4 amp. and 7.5 volts, the cadmium separated in small crystalline scales, which, during washing, became detached. Experiments were made using less acetic acid, lower current and less voltage and at various temperatures, but the results were not satisfactory. The deposition was not quantitative from the sodium phosphate solutions containing free phosphoric acid.

Eliasberg[63] found that cadmium was not completely precipitated from cold solutions of the cadmium acetate or sulphate with 2–3 gm. sodium acetate and a few cc. of acetic acid. The current had to be maintained at 0.04–0.06 amp. for 4 hours to deposit all of the cadmium. Fair results were obtained.

[64] Am. J. Sci., (4) **20**, 273 (1905).
[65] Ber., **11**, 2048 (1878); Am. J. Sci., (3) **17**, 60 (1879); Am. Phil. Soc. Pr., **18**, 46 (1878).
[66] Z. anal. Chem., **19**, 1 (1880).
[67] Ber., **29**, 1585 (1896).

Warwick[68] deposited cadmium from formate solutions. Cadmium formate, prepared by dissolving cadmium carbonate in formic acid, crystallized with two molecules of water. A current of 0.11–0.13 amp. deposited 0.04–0.1 gm. of cadmium in 7 hours from a solution containing 10–15 percent of free formic acid. The deposit, which was almost quantitative, was firm and adherent, white in color, with a bright metallic luster. With up to 5 cc. of free formic acid the deposits were failures. With 5 cc. of free formic acid the deposits were compact. The metal deposited faster at higher temperatures, but there seemed to be an increase in the amount of sponge. With a low current (0.07 amp.) and 15–25 cc. of free formic acid the results were fairly accurate. Cadmium could be separated from zinc, but not from copper in this solution. In the latter case, both metals precipitated together as a very dark spongy deposit. Good separations could not be made from iron, cobalt or nickel.

Avery and Dales[69] added 6 cc. of formic acid (1.2 sp. gr.) to the cadmium sulphate solution, then potassium carbonate until a slight permanent turbidity was produced, and finally enough formic acid to dissolve the turbidity, plus 1 cc. in excess. The solution was diluted to 150 cc. and electrolyzed with 0.15–0.2 amp.

Balachowsky[7] used 5–7 cc. of acetic acid with 1.5–2 gm. of cadmium sulphate. The solution was heated to 60° and electrolyzed with a current of 0.04–0.06 amp. The deposited cadmium was pure, crystalline and adherent.

Exner[9] used an acetate solution with a rotating anode.

Flora[26] deposited cadmium from acetate solutions with a rotating cathode, using the same composition of solutions that Exner employed with the rotating anode. The solutions, prepared by adding 1.5 gm. sodium acetate and 0.5–1 gm. potassium sulphate to increase the conductivity to 0.14 gm. cadmium in 60 cc. of solution, gave less satisfactory deposits than those made by adding 0.2 gm. sodium hydroxide to the cadmium sulphate and then dissolving the precipitate in a slight excess of acetic acid. Not more than 0.15 gm. of cadmium could be deposited. A current higher than 0.3 amp. produced a spongy deposit. The deposit

[68] Chem. News, **66**, 255 (1892); Z. anorg. Chem., **1**, 258.
[69] J. Am. Chem. Soc., **19**, 380 (1897).

was "rather crystalline, fairly compact and easily washed." The cadmium as chloride or nitrate behaved differently. Unsatisfactory results were obtained with formate solutions. "When potassium formate was present in even the smallest amounts the precipitate was spongy and non-adherent." From solutions containing formic acid alone the metal deposited in a satisfactory form, but only after long passage of the current. Solutions containing ammonium tartrate also gave spongy deposits. The use of tartaric acid alone gave fairly satisfactory results with a current of 1.5 amp.

Davison[70] employed an anode rotating 580 times per minute, in the deposition of cadmium from various organic electrolytes. The time of deposition was from 4–15 minutes with 5 amp. From a solution containing 0.29 gm. of cadmium as sulphate, 1.2–5 gm. of sodium carbonate and 5–16 cc. formic acid (1.06 sp. gr.) the cadmium "was completely precipitated as a dark gray, spongy, though adherent deposit." Ammonium formate in place of the sodium formate gave a similar result. Sodium acetate or ammonium acetate (3 gm.) with free acetic acid (0.25 cc.) proved to be very like the formate electrolyte. An ammoniacal solution was inferior to a slightly acid solution, the deposition being incomplete. The appearance of the deposit was not given. The deposition from sodium or ammonium lactate solutions was incomplete. Ammonium or sodium succinate solutions gave excellent deposits similar to the formate and acetate. A good separation was obtained from magnesium in the formate bath.

Holmes,[71] with a rotating anode, deposited cadmium from solutions containing 1 gm. ammonium acetate, 0.5–1 cc. acetic acid (1:3) and 0.2 gm. cadmium sulphate; 0.15–0.3 amp. was used. A preliminary heating of the electrolyte was necessary, "influencing the character of the deposit to a considerable extent." From a cold solution "the deposit contained coarse crystals" having a "tendency to sponginess and hence occluding mother liquor." Good separations were obtained from aluminum, magnesium and manganese, but not from chromium, zinc, nickel, ferrous or ferric iron.

Holmes and Dover,[72] and Dover,[73] tried separations of cadmium

[70] J. Am. Chem. Soc., **27**, 1275 (1905).
[71] J. Am. Chem. Soc., **30**, 1865 (1908).
[72] J. Am. Chem. Soc., **32**, 1251 (1910).
[73] J. Am. Chem. Soc., **33**, 1577 (1911).

from alkaline earth metals, using acetate, formate and lactate electrolytes. A rotating anode was used. With high current densities (5 amp.) the deposits of cadmium were "dark in color, spongy and non-adherent, difficult to dry, and in most cases evidently not worth weighing," whether cadmium was used alone or in presence of other metals. With low currents, interesting and accurate results were obtained.

"During this work it has been evident that each variety of ion present in the solution exerts a very definite influence upon the deposit. The presence of two ions in a solution may produce a decidedly different deposit from that obtained by the influence of either ion alone. For instance, in the previous work conducted with cadmium sulphate solutions, with sulphuric acid electrolyte, smooth, adherent deposits of fine crystalline structure were obtained. The deposits from a cadmium sulphate solution using the acetate electrolyte were mostly coarsely crystalline, and if another metal were present, *e. g.*, aluminum, the crystals tended to sponginess and therefore to the occlusion of mother liquor unless carefully washed with hot water. These same conditions were observed when a cadmium acetate solution was used with the acetate electrolyte, so that in general it may be said that the sulphate ion aids in forming a finely crystalline, compact deposit, while the acetate ion caused the deposit to be more coarsely crystalline, with a tendency to sponginess. The presence of the sulphate ion always seems to improve the character of the deposit, no matter what other ion may be present."

Quantitative deposits of cadmium were obtained with a current of 0.3 amp. from a solution containing 2 gm. ammonium acetate, 1 cc. acetic acid, 0.17 gm. of cadmium as acetate, in 120 cc. The presence of alkaline earth acetates seemed to be without influence. The use of cadmium sulphate in place of the cadmium acetate gave deposits which "were clean and smooth, with few crystals of any size, easily washed and dried, showing the valuable influence of the sulphate ion." The presence of calcium was without influence. The other alkaline earths could not be added, due to the insolubility of their sulphates. The presence of the acetic acid hindered the complete precipitation of the cadmium. Under similar conditions, using formate and formic acid, the deposits were crystalline and adherent and of good color, but very careful

washing was necessary, particularly when alkali earth metals were present. When cadmium sulphate was used in place of the cadmium formate, "very excellent deposits were obtained, showing again the influence of the sulphate ion." Some free formic acid was necessary in the electrolyte to prevent the precipitation of difficultly soluble cadmium formate. "The results on the whole were better than when the acetate electrolyte was used alone." The addition of the acetate ion, *i. e.*, the use of cadmium acetate instead of cadmium formate, gave "finely crystalline and adherent, but slightly porous deposits, which were less firm than when the sulphate ion was present." Similar experiments with the lactate electrolyte gave deposits which were mostly "fine and adherent," but there were also "coarsely crystalline plates which scaled off and were not easily handled." The presence of the sulphate ion resulted in the formation of "a very excellent deposit" which was "silvery-white, very finely crystalline, clean and easy to wash." The addition of the acetate ion did not give any better deposit than the lactate ions alone. The addition of formate ions improved the deposits, but coarse "crystalline plates which scaled off in washing" were again formed. The addition of sulphate ions to the lactate bath gave the best deposits. These organic electrolytes, arranged in the order in which the most cadmium could be deposited without the formation of loose crystalline scales, are: Formate in formate, formate in acetate, lactate in formate, lactate in lactate, formate in lactate, acetate in acetate, acetate in formate, lactate in acetate and acetate in lactate. The quantity of cadmium varied from 0.19 to 0.08 gm. The deposit seemed to be "finer and more adhesive when the solution was decidedly acid." Too much acid made it very difficult to deposit the last traces of the metal.

III. (c) Tartrate solutions.

Smith and Knerr[74] separated cadmium from zinc in a hot solution containing 2 gm. of sodium tartrate and an excess of tartaric acid. Best results were with 0.045 amp., which deposited the 0.006 gm. of cadmium in 45 minutes. The current was changed some without influencing the results.

[74] J. Am. Chem. Soc., 8, 206 (1886).

Sand[75] used the constant potential method for the rapid separation of metals. As a rule the solutions were electrolyzed hot with an initial current of 3–5 amp. and a final current of about 0.2 amp. The volume of the solution varied from 85–130 cc., and the time of electrolysis from 5–15 minutes. With cadmium the best results were obtained from a cold nitrate solution containing sodium tartrate, which was rendered ammoniacal near the end of the electrolysis. Separation from zinc was performed in acetate solutions containing free acetic acid; from lead and bismuth by depositing these from solutions containing free nitric acid. Bismuth may also be deposited from cadmium in tartrate solutions containing only free tartaric acid.

IV. COMMERCIAL PLATING OR REFINING.

In 1849 the Russell and Woolrich[76] process was patented. Forty parts of metallic cadmium or 100 parts of cadmium nitrate was dissolved in nitric acid and precipitated with a 10 percent solution of sodium carbonate. The precipitated carbonate was washed 4–5 times with hot water, and then dissolved in just sufficient amount of strong potassium cyanide. A 10 percent excess of potassium cyanide and sufficient water to make 1,000 parts were added. The bath was used at a temperature of 100° Fahr. (38° C.). This bath gave a white reguline metal when operated at 3–4 volts. The bath should not be allowed to become weak in metallic content. A large excess of potassium cyanide has a decided tendency to produce roughness of the deposit. "It is advisable to employ as low a voltage as possible, otherwise the deposit is liable to be rough and crystalline."

Mylius and Fromm[77] purified cadmium containing zinc by using it as anode in a very dilute salt or acid solution with a platinum or pure cadmium cathode. Both cadmium and zinc dissolve from the anode, but only the cadmium is deposited upon the cathode. Cadmium containing lead was refined in a concentrated solution of cadmium sulphate. The best current density is between 0.5 and 1 amp. The formation of spongy metal is

[75] J. Chem. Soc., **91**, 373 (1907) and **93**, 1572 (1908); Pr. Chem. Soc., **23**, 26 (1907); Trans. Faraday Soc., **5**, 159.

[76] Macmillan, A Treatise on Electrometallurgy, 258, and Barclay and Hainsworth, Electroplating, 323 (1912).

[77] Z. anorg. Chem., **13**, 157 (1896), thru. Jahr. Ber., 520 (1896).

not so apt to occur as with zinc, and may be entirely avoided by good stirring and by maintaining slight acidity of the electrolyte. The cathodes easily become rough. The cathodes were melted and sublimed in a vacuum, thus producing cadmium in which the metallic impurities were less than 0.001 percent.

Cowper-Coles[78] says that cadmium alloys have been deposited on a commercial scale. An alloy containing a small percentage of silver is employed for coating bright steel parts of machines, whilst domestic articles are plated with an alloy containing 7.5 percent silver. Such alloys have been found to withstand tarnishing much better than pure silver or standard silver containing 7.5 percent copper. Very careful adjustment of the concentration of the solutions and the current density seems to be necessary for obtaining a definite composition of the electrodeposited alloy; and, moreover, if the bath is to be maintained for any length of time in working condition, the deposit must be of the same composition as the anode.

Fischer[79] prepared a solution for plating iron objects with cadmium by dissolving 32 gm. of cadmium chloride in 0.5 liter of water and by precipitating with sodium carbonate. The precipitate was well washed with water and dissolved while still moist in a solution of 50 gm. potassium cyanide in a liter of water. The bath should be used at 40° C. Cadmium anodes should be used, and 4–5 volts applied. The deposit after buffing is the same color as tin, but rather harder.

Basset[80] deposited cadmium from a cold solution of 5 oz. potassium cyanide, 1.7 oz. cadmium carbonate and 1 gal. water with a current pressure of 2 volts. The cadmium carbonate should be freshly precipitated from a solution of cadmium sulphate in water or metallic cadmium in nitric acid. The deposit is soft and white, and may be given a high polish, which it retains about as well as nickel. It may be plated directly on steel or iron, where it is more rustproof than nickel or tin and equal to an electrodeposited zinc plate. A good antique finish may be obtained, and the surface may be oxidized in a black nickel solution, but not in arsenic and sulphur dip.

[78] Electrochemist and Metallurgist, 3, 582 (1904)—thru J. Soc. Chem. Ind., 23, 446 (1904), and "Mineral Resources of the United States for 1908."

[79] Chem. Ztg., 28, 1209 (1904), thru. J. Soc. Chem. Ind., 24, 34 (1905).

[80] Metal. Ind., 9, 509 (1911).

Marino[81] added boro-citrate to the double ammonium cadmium sulphate. The salt was then heated, and after cooling received a second addition of a reducing agent such as glucose with citric or tartaric acid (3 parts citric or 2 parts tartaric acid to 1 part of glucose). This treatment produced complete dissociation, and thus the deposition could be made with a weak current.

Borchers[82] precipitated compact deposits of cadmium from its solutions in laboratory experiments with a current density of 6–14 amp. per sq. ft. (0.66–1.55 amp. per sq. dm.).

Brand[83] purified cadmium contaminated with zinc and various other metals by electrolysis in a solution of cadmium sulphate containing 0.8 lb. cadmium per gallon (100 gm. per liter) and 5 percent free sulphuric acid. The anodes were of cast cadmium, containing cadmium, 88.7 percent; zinc, 8.55 percent; lead, 1.45 percent, and copper, 1.35 percent. With the electrodes 2 in. (5.1 cm.) apart, and a current density of 12.8 amp. per sq. ft. (1.4 amp. per sq. dm.), the tension of the bath was only 0.042 volt, because the solution of the zinc, which remained in the electrolyte, introduced a considerable amount of electric energy into the circuit. The tension increased to 0.048 volt as soon as the solution contained, together with the 5 percent sulphuric acid, 0.464 lb. of zinc and 0.04 lb. of cadmium per gallon (57 and 5 gm. per liter, respectively).

Cadmium plating is treated very briefly in the books[84] on electroplating and refining. The cyanide methods which are given above are recommended. Judging from these books there is very little commercial plating of cadmium.

Indiana University,
Bloomington, Indiana.

[81] Eng. Pat., **24**, 562 (1913).

[82] Electrometallurgie, 298 (1895) and 451 (1903).

[83] Dammer, Chem. Technol., **2**, 33 and 687.

[82] and [83] Thru Schnabel and Louis "Handbook of Metallurgy," **2**, 328 (1907).

[84] Barclay and Hainsworth, Electroplating" (1912); Field, "Principles of Electrodeposition" (1911); Macmillan-Cooper, "Electrometallurgy" (1910).

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

ELECTRODEPOSITION OF CADMIUM

PART II.—EXPERIMENTAL

By Frank C. Mathers and Hugh M. Marble.

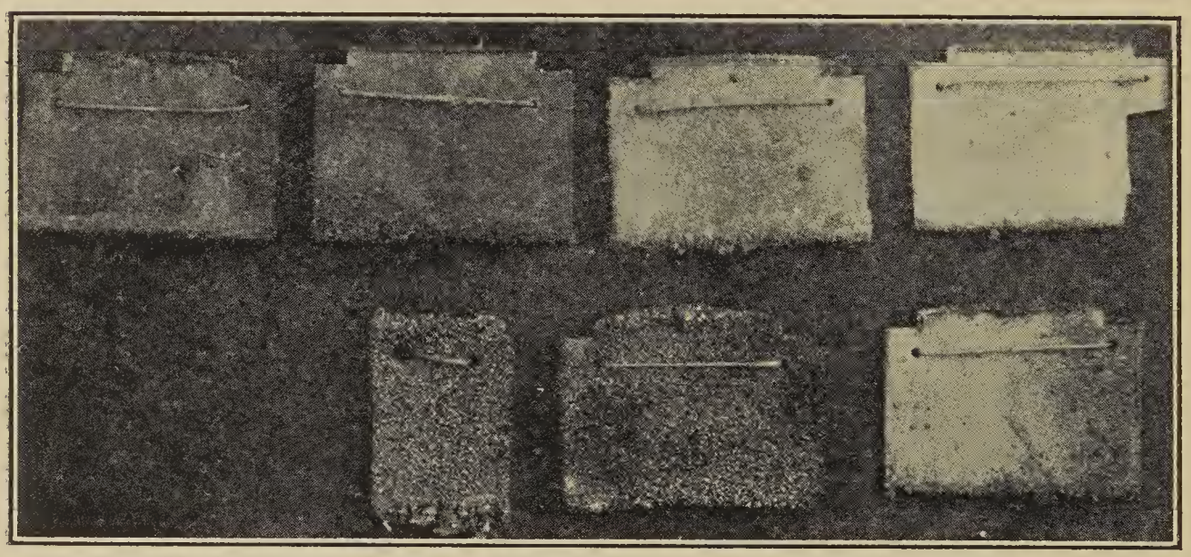
The descriptions of electrodeposited cadmium found in electrochemical literature show that the deposits were always crystalline and that only small quantities of cadmium could be deposited without the formation of projections or rough crystals which soon produced short-circuits. Neumann says that cadmium shows a pronounced tendency to form rough crystalline or spongy deposits, and that 0.15 gm. is the maximum quantity that can be deposited in a smooth quantitative condition from any but a cyanide solution. Cyanide solutions of many metals have the peculiar property of giving smooth, non-crystalline deposits of the metals. Some writers think that the cyanide or other organic solution decomposes during electrolysis, with the formation of colloidal substances which act as "addition agents" in preventing rough crystalline deposits.

In view of the smooth deposits of lead which have been obtained by the use of addition substances, it seemed reasonable to us to suppose that cadmium could be deposited from any of the ordinary salts of cadmium, with the use of the proper addition agents, in as good a condition as lead is deposited. These experiments were undertaken with the idea of obtaining information concerning the general question of the effect of the composition of the bath upon the character of the deposited metal.

Manipulation. Beakers of 225–250 cc. capacity were used as electrolyzing vessels. The volume of the electrolyte was 200 cc. in each experiment. Each bath always contained cadmium salts equivalent to 4 percent metallic cadmium. Cathodes, made from sheets of metallic cadmium which had been rolled in a cornet machine, were suspended in the beakers with strips of the same

rolled cadmium. The cathodes were 4.2 by 6 cm., giving a total area of 50 sq. cm. The current strength was 0.2 amp., which was a current density of 0.4 amp. per 100 sq. cm. (3.6 amp. per sq. ft.). The current was obtained from storage batteries, consequently electrolysis was continuous. Two anodes and one cathode were used in each electrolyzing vessel. The anodes, 4 by 4 by 1 cm., were cast in a graphite mold. Connections were made to the anodes by small copper wires passing through holes which had been made in the anodes at the time of casting.

A B C D



E F G

FIG. 1. CHLORIDE BATHS.

Each 200 cc. bath contained 8 gm. cadmium as chloride, 20 gm. ammonium chloride, 2 to 10 cc. hydrochloric acid and

A. 0.2 gm. peptone and 20 gm. aluminum chloride.
B. 0.2 gm. peptone.
C. 0.2 gm. peptone.
D. 0.2 gm. peptone and 20 gm. ferric chloride.
E. 0.2 gm. glue.
F. 0.2 gm. isinglass.
G. 0.2 gm. peptone and 20 gm. manganese chloride.

The solutions were stirred at intervals with a stirring rod, but no attempt was made to continuously circulate or agitate the electrolytes. The anodes were usually wrapped in filter papers to keep anode slime from mixing into the bath. A better way to avoid the slime is to amalgamate the anodes.

Sulphate Solutions: Each 200 cc. bath contained 8 gm. (4 percent) of cadmium as sulphate. About 2.5 percent of free sulphuric acid seemed to be the best amount, although variations from this amount did not have much effect upon the character

of the deposit. However, with no free acid in the bath there was a much greater tendency towards the formation of spongy deposits. The addition of ammonium sulphate also lessened the formation of sponge.

With only 0.5 cc. of sulphuric acid and no addition substance, the deposit was crystalline and non-adherent, with trees or projections on the edges. The addition of 0.2 gm. of peptone to this bath gave spongy, non-adherent deposits after the bath had run for a few hours. A bath containing 20 gm. ammonium sulphate, 0.2 gm. peptone and 5 cc. sulphuric acid gave deposits which were dark in color, but not loose and spongy.

With 1 cc. sulphuric acid and 1 gm. of glue the deposits were always dark and spongy, either with or without the addition of ammonium sulphate.

Clove oil, 4 drops, or gum arabic, 0.2–10 gm., in baths containing 1 cc. sulphuric acid and 20 gm. ammonium sulphate or sodium chloride, seemed to have very little effect. The deposits were coarsely crystalline and rough.

The sulphate baths were very unsatisfactory. They seemed to give spongy deposits more easily than the other baths.

Phosphate Solutions: A bath containing 8 gm. (4 percent) cadmium as phosphate and 10 cc. free phosphoric acid gave a crystalline, poorly adherent deposit. After the addition of 0.2 gm. peptone the deposit was very good, but it gradually became rough, and was very irregular at the end of the experiment. The addition of 20 gm. of ammonium chloride or ammonium perchlorate to baths of the above composition did not change the results materially.

Although phosphate baths are seldom used in plating, the results with these phosphate solutions were encouraging. The deposits were better than in the case of the sulphates.

Chloride Solutions: Each 200 cc. bath contained 8 gm. (4 percent) of cadmium as the chloride. Experiments with forty different baths failed to show a single smooth, non-crystalline deposit. There was a tendency towards the formation of a spongy deposit in the absence of free hydrochloric acid. Variation in the amount of free acid had very little effect upon the deposit, providing there was enough present to prevent the

spongy deposits. In almost all cases the deposits were crystalline, rough and often poorly adherent. The addition of ammonium chloride or sodium chloride produced better deposits with less tendency toward sponginess.

Peptone, 0.2 gm., with 20 gm. of ammonium chloride in the solution, produced the best deposits. There was always a tendency for the peptone to give spongy places upon the cathode, especially upon the bottom or where a stirring rod touched the

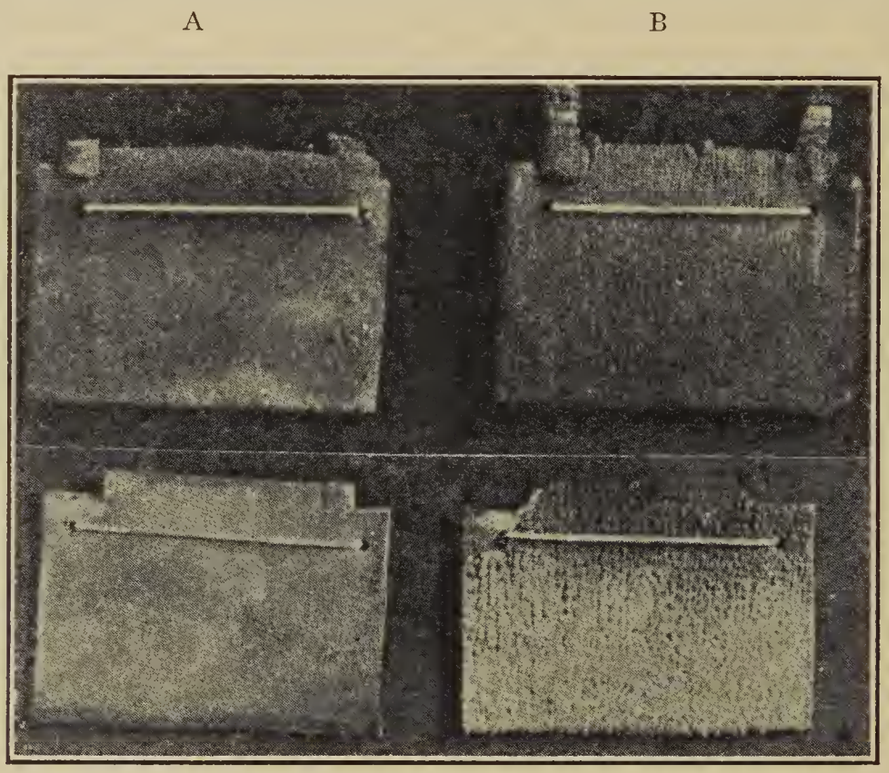


FIG. 2. FLUOBORATE AND FLUOSILICATE BATHS.

Each 200 cc. bath contained:

A. 0.2 gm. peptone, 8 gm. cadmium as fluoborate and 2 gm. free fluoboric acid.
B. 0.1 gm. phloridizin, 8 gm. cadmium as fluoborate and 2 gm. free fluoboric acid.
C and D. 0.2 gm. peptone, 8 gm. cadmium as fluosilicate, 8 gm. free fluosilicic acid.
(A rough deposit, like D, was often obtained from a new solution, which afterwards gave a smooth cathode, like C.)

cathode. The larger the amount of peptone and the smaller the amount of free acid, the greater the tendency towards sponginess. Consequently the addition of free acid seemed to make the deposits a little better. The addition of 2 cc. nitric acid caused a deposit to become spongy in a solution which had been giving a bright but crystalline deposit. All of these deposits were crystalline and rough on the edges, with some spongy places. The use of ammonium perchlorate, ammonium fluo-

borate or calcium chloride in place of the ammonium chloride did not improve the deposits.

With 1 gm. of glue or isinglass and 0.5 cc. hydrochloric acid the deposit was spongy. With the addition of 20 gm. ammonium chloride to this bath the deposit became coarsely crystalline. With 0.2 gm. glue, 2 cc. hydrochloric acid and 20 gm. ammonium chloride the deposits were bright and crystalline. Glue had a very much less beneficial action than the peptone.

Clove oil, which had such a marked beneficial action in the lead perchlorate and lead fluosilicate baths, was apparently without effect in these cadmium chloride solutions. From 2 to 40 drops of clove oil, with or without free acid or ammonium chloride, produced the same coarsely crystalline, rough deposits. There seemed to be no tendency towards the formation of sponge.

Gum arabic 2–10 gm., nitrobenzene 4 drops, alcohol 10 cc., glycerine 4 drops, dextrine 2.6 gm., or resorcine 0.2 gm., showed no action either in preventing crystallization or in causing sponginess. These addition substances were tried both with and without free acid and ammonium chloride. In one experiment with the gum arabic, 20 cc. of free hydrochloric acid was used, and in another case sodium chloride was used in place of the ammonium chloride, but no good deposits were obtained.

A number of addition substances containing tannin and belonging to a group which might be called vegetable extracts had a pronounced tendency to produce spongy deposits. This was especially true of tannin, 0.2 gm. of which, in the presence of 20 gm. of ammonium chloride, gave a spongy deposit even after 12.5 cc. of hydrochloric acid had been added. The solution never gave a bright deposit even after running several days. Licorice extract 0.2 gm., pyrogallol 0.2 gm., succotrin aloes 0.2 gm., or the mucilage extracted from 5 gm. of flaxseed by standing over night in water, gave loose, almost spongy deposits, although there were intervals when the cathodes seemed to be bright.

The best deposit was obtained from a bath containing 20 gm. ammonium chloride, 15 cc. hydrochloric acid, 0.2 gm. peptone and 15 gm. crystallized ferric chloride. The deposit was dense, smooth and very finely crystalline. There was no indication of

rough projecting crystals until after electrolysis for several days. The green color of the solution showed that the iron was reduced. Three times during the run the bath was heated, and bromine water was added until the iron was completely oxidized. It was not determined whether this was necessary or not. Once during the run 5 cc. hydrochloric acid and 0.2 gm. peptone were added. No bath of this composition minus the peptone was tried. Aluminum, manganese or chromium chlorides did not produce

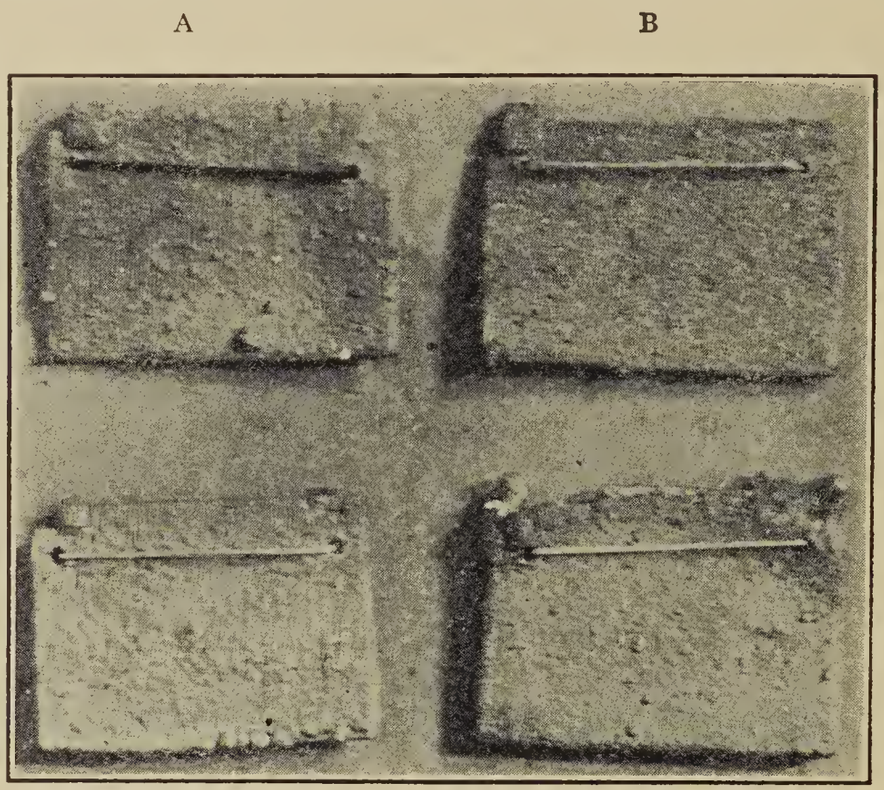


FIG. 3. PERCHLORATE BATHS.

Each 200 cc. bath contained 8 gm. cadmium as chloride and
A and B. 0.2 gm. peptone and 8 gm. free perchloric acid.
C. 3 drops of clove oil and 8 gm. free perchloric acid.
D. 0.2 gm. peptone and 2 gm. free perchloric acid.

as good deposits as the iron chloride. Colorimetric analysis of the cathode showed 0.00268 percent of iron.

Nitrate Solutions: Nitrate baths could not be electrolyzed in the same way as the other baths. The copper wires used in making connections to the anodes and the cadmium strips holding the cathodes were corroded or dissolved so that the electrical connections were broken. Attempts to obtain deposits from these solutions were abandoned.

Alkaline Solutions: A 200 cc. bath containing 8 gm. (4 percent) of cadmium as chloride, 20 gm. ammonium chloride, 0.2 gm. peptone and enough ammonium hydroxide to redissolve the precipitate and to give a clear solution, produced a very spongy deposit. Platinum wires had to be used for making anode connections on account of the corrosion of the copper wires. A basic cadmium salt formed upon the anodes.

Cyanide Solutions: A bath containing 8 gm. (4 percent) cadmium as potassium cadmium cyanide and 1 gm. of potassium cyanide, which was afterwards increased to 18 gm., gave a fine, smooth deposit except for feathers upon the edges of the cathode, which showed that the current density was too high for the cyanide solutions.

Bromide Solutions: A bath containing 8 gm. (4 percent) cadmium as the bromide, 15 gm. potassium bromide and 0.1 gm. peptone gave a coarsely crystalline, rough deposit like that from the chloride solutions.

Iodide Solutions: A bath containing 8 gm. (4 percent) cadmium as the iodide, 5 gm. potassium iodide and 1 gm. peptone produced a deposit similar to those from the bromide and chloride baths.

Acetate Solutions: No good deposits could be obtained from acetate solutions. Electrolysis of cadmium acetate gave a crystalline, brittle, non-adherent deposit. Addition of 8 gm. ammonium perchlorate made the deposit a little firmer. The deposit was also improved by the addition of 1 cc. acetic acid, but 10 cc. made no further change. The addition of 0.4 gm. peptone to this bath gave a fair deposit except for rough edges and spongy spots. The peptone gave spongy deposits except when the large amounts of acetic acid (10 cc.) were used.

A mixture of 20 gm. ammonium chloride or ammonium perchlorate, 5 cc. acetic acid and 0.05 gm. succortrin aloes and cadmium acetate equivalent to 8 gm. cadmium was heated to boiling, cooled and filtered. The deposits from these solutions were spongy and of no value.

Fluosilicate Solutions: A solution similar to the one used by Senn, containing 8 gm. (4 percent) cadmium as sulphate and

4 percent fluosilicic acid, gave a flaky, bright, non-adherent deposit which dropped to the bottom of the beaker. Addition of 6 drops sulphuric acid made the deposit a little firmer. With the further addition of 0.1 gm. of glue the deposit became dark, partly spongy and poorly adherent. The results from this bath were not satisfactory, being but little better than when the fluosilicic acid was not present. The further addition of 0.2 gm. peptone gave a bulky, spongy deposit.

A bath containing 8 gm. cadmium as fluosilicate, 10 gm. fluosilicic acid and 0.2 gm. peptone gave a non-crystalline deposit, but the surface was rough, being thickly covered with

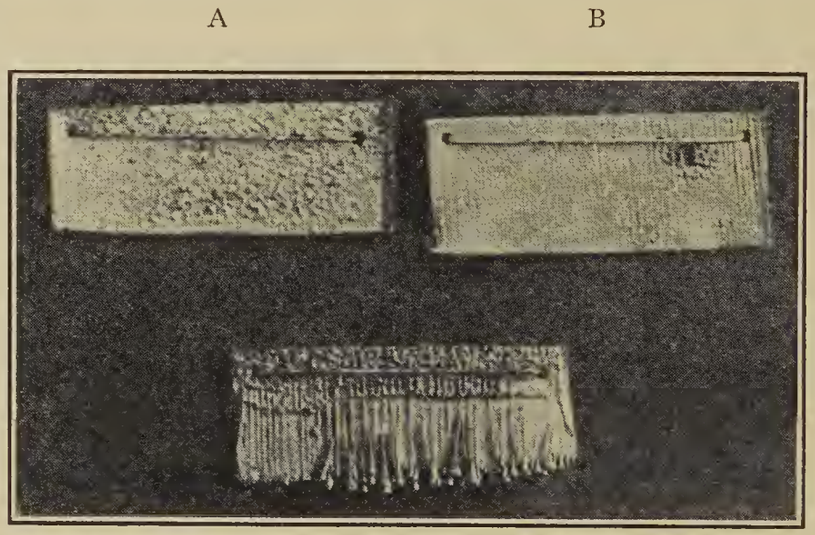


FIG. 4. FLUORIDE BATHS.

Each 200 cc. bath contained 8 gm. cadmium as fluoride, 8 gm. free hydrofluoric acid and

A. 0.2 gm. glue.
B and C. 4 drops of clove oil.

little, smooth bumps. After three days a new cathode was introduced. The deposit was smooth and non-crystalline, but on one side there was a spongy place, which finally grew until it covered almost half of that side. After electrolysis for two weeks the amount of free acid was 1.04 percent.

Perchlorate Solutions: The addition of ammonium perchlorate to chloride baths did not give good results.

A bath containing 8 gm. (4 percent) cadmium as the perchlorate, 7 percent free perchloric acid and 0.2 gm. peptone gave a very fine, dense deposit. Addition of 0.2 gm. more of peptone caused the deposit to become spongy, but after awhile the bath

again gave a nice, bright, smooth deposit. A bath like the above, except that only 1 percent free perchloric acid was present, gave just as good a deposit, and after eight days there was no indication of a lack of free acid.

Clove oil, 3 drops, gave a little brighter but a rougher deposit than the peptone. However, there was no tendency towards the formation of sponge.

Glue, 0.1 gm., gave almost as good a deposit as the clove oil, except for a greater tendency toward spongy formation.

To the bath containing the clove oil, 2.5 percent of iron as perchlorate was added. The deposit was bright, but there was no indication that the iron was of any special value.

These results show that the ion ClO_4 has a very beneficial action upon the character of the cadmium deposit. Peptone, clove oil or glue can be used as addition agents.

Fluoborate Solutions: Lead fluoborate solutions have been used in lead deposition with better results than lead fluosilicate solutions. Fluoboric acid is very easily made by adding hydrofluoric acid to boric acid in a platinum dish. The reaction is very vigorous, and all of the hydrofluoric acid will be combined if a slight excess of the boric acid is used.

Excellent deposits were obtained from solutions containing 4 percent of cadmium as fluoborate, 1–6.4 percent of free fluoboric acid and 0.2 gm. of peptone.

Phloridizin, 0.1 gm., in a solution containing 1 percent of free acid, gave the best deposit that was obtained in any of the experiments. Phloridizin is a glucoside obtained from the root bark of apple trees. It was found to give good deposits of lead from perchlorate solutions.

Fluoride Solutions: Baths containing 4 percent of cadmium as the fluoride, 15 percent of free hydrofluoric acid and 0.2 gm. of glue or 4 drops of clove oil gave excellent results. The deposits were exceptionally bright and firm, but sometimes rough and peculiarly striated. There was also a tendency for parts of the cathodes to be spongy. The three addition agents, peptone, glue and clove oil, were about equally efficient.

Current Efficiency: Two baths, one containing 4 percent cadmium as perchlorate, 1 percent free perchloric acid and 0.2 gm.

peptone, and the other containing 4 percent of cadmium as fluoborate, 1 percent free fluoboric acid and 0.1 gm. phloridizin, were run in series with a copper coulometer. The quantitative results are:

	Volts	Anode Loss		Cathode Gain	
		Weight	Percent	Weight	Percent
Copper coulometer . . .	. . . .	. . . .	. . .	9.4599	. .
Cadmium (perchlorate)	0.22 – 0.20	16.8196	100.55	16.7401	100.08
Cadmium (fluoborate) .	0.32 – 0.18	16.8076	100.48	16.7250	99.99

The anodes were amalgamated to prevent the loss of slime. These results upon the current efficiency are remarkably close to the theoretical value, taking the copper coulometer as the standard.

SUMMARY.

Part I of this paper furnished an historical review of the electrodeposition of cadmium. In almost all cases crystalline, rough deposits had been obtained.

Part II is experimental work on the electrodeposition of cadmium. An attempt was made to determine what salts of cadmium are best suited for giving smooth, non-crystalline deposits. Baths containing equivalent weights of the different salts of cadmium were electrolyzed under the same conditions. The cathodes from the ammoniacal and the alkaline tartrate baths were hopelessly spongy. The deposits from the acetate, bromide, iodide, sulphate, phosphate and chloride solutions were rough and crystalline. Many experiments were tried with the chloride solutions. A bath containing 4 percent cadmium as the chloride, 10 percent ammonium chloride, 5 percent hydrochloric acid (by volume) and 0.1 percent peptone gave a fairly smooth, finely crystalline deposit. A bath of the same composition as that just given, with the addition of 10 percent ferric chloride, gave a much better deposit. Manganese, aluminum or chromium chlorides did not improve the deposit in the same way that the iron did. None of these deposits were equal to those described below. In the few experiments that were tried with the bromide and iodide solutions, the deposits were more crystalline and rough than with the chloride baths.

Fluoride, fluosilicate, fluoborate or perchlorate solutions containing 4 percent cadmium, with 0.5–5 percent free acid and 0.2 gm. peptone, glue or phloridizin, or 4 drops of clove oil, gave excellent, smooth deposits. Not all of these addition substances were tried with all of the above cadmium salts, but in all cases where they were tried excellent deposits were obtained. Sometimes spongy places or spots were formed upon the cathodes. Some rough projections also gradually formed on some of the cathodes. It is thought that these rough places were produced by particles of slime, which became detached from the anodes in spite of the wrappings of filter paper. Amalgamation of the anodes completely prevented slime from becoming detached, but this scheme was tried only in the quantitative experiments.

These experiments again demonstrate the value of "addition agents," since smooth deposits of cadmium could not be obtained without their use. The same addition substances—clove oil, glue, peptone and phloridizin—which were found to give good lead deposits are the only valuable ones for cadmium deposition.

Cadmium is much more difficult to obtain in a smooth condition than lead.

There was a gradual loss of free acid in the baths, due to chemical solution of the anode. This had little effect upon the deposits, since only a little free acid is required in the solutions.

Discussion of Results.

Excepting the smooth deposits of cadmium which Senn obtained from a fluosilicate bath containing some sulphate and small amounts of glue, no thick, non-crystalline deposits have been obtained from solutions of any cadmium salts. The records show that only very small amounts of cadmium could be deposited in quantitative work without the formation of loose crystals or scales or sponge.

Some critics have said that the lead salt of perchloric or fluosilicic or fluoboric acid gave good deposits simply because these acids were strongly dissociating and non-oxidizing. The idea that these acid ions themselves had any specific action in causing the smooth deposits has not been well received. When Mennicke made experiments upon the refining of tin in a fluo-

silicate bath, a reviewer said[1] that as good deposits would probably have been obtained with some other strong, non-oxidizing acid in the place of the fluosilicic acid, and that the only advantage of fluosilicic acid in lead deposition was that a soluble salt was produced.

This hypothesis that perchloric, fluoboric and fluosilicic acids possess no special value in lead deposition over sulphuric, hydrochloric and hydrobromic acids, except that they form soluble salts, cannot be tested experimentally in the case of lead. Such a hypothesis can be tested in the case of cadmium because almost all of the cadmium salts are soluble.

A number of the experimenters have mentioned an important observation which bears upon this point, but Miss Holmes first definitely stated the general rule that "All ions in the solution have a definite action upon the deposit." She proved this very conclusively in the case of the SO_4 ions, which greatly improved the deposits from cadmium acetate solutions. Is this a specific property of the SO_4 ions, or would other acid ions as Cl, Br, ClO_4, etc., have shown the same beneficial effects? If this were a specific property of the SO_4 ion itself, and not merely the effect of a strongly dissociating salt, another ion might be found which would exercise a very much more beneficial action and give a much better deposit. On the other hand, there might be ions which would have the opposite action and would tend to produce rough or spongy deposits whenever they were present.

The author feels that a good deposit is the result of the additive properties of the acid ion and the addition substance. A stronger statement of the theory as given before[2] is that any metallic salt will give a good deposit if the proper addition agent is used. Peptone produced a much better deposit of cadmium from chloride solutions that did glue or isinglass. Clove oil seemed to be almost without effect. See Fig. 1. Can this mean anything else than that the additive properties of the peptone and the chloride ions almost produced the conditions required for giving a good deposit, and that the glue and, still more, the clove oil failed to have the specific properties required to supplement those of the chloride ions? In these experiments no addi-

[1] Electrochem. Met. Ind., **4**, 25 (1906).
[2] Trans. Am. Electrochem. Soc., **24**, 315 (1913).

tion substance was found which perfectly satisfied the conditions required by the chloride ions, but a more extended research would perhaps detect the correct substance. No addition substance was found which helped very much in the sulphate baths. This means to me that the addition substances which we have been using do not supplement the specific properties of the SO_4 ions to produce conditions which are required for smooth cadmium deposits. All of these addition agents, glue, peptone, clove oil and phloridizin, which would not produce smooth deposits from the chloride, bromide, sulphate, iodide, acetate and phosphate solutions, do produce good, smooth deposits of cadmium from perchlorate, fluosilicate, fluoborate and fluoride solutions. Considering that all of these experiments were tried under exactly the same conditions of current and concentration, there must be some specific property possessed by fluoride, fluosilicate. fluoborate and perchlorate ions which supplements the specific properties of the addition substances, clove oil, glue, peptone and phloridizin, and that the other acid ions, as chloride, sulphate, phosphate, etc., lack this specific property, at least as far as cadmium is concerned.

The theory that a strongly dissociating acid must be the basis of any satisfactory bath does not hold in the case of cadmium. Some of the strong acids, *e. g.*, hydrochloric acid, and of the weak acids, *e. g.*, phosphoric acid, formed baths which gave poor deposits. Two acids of medium and approximately equal strength, *e. g.*, sulphuric and hydrofluosilicic acid, act differently in the baths, the former giving poor deposits, and the latter good deposits.

Indiana University,
Bloomington, Indiana.

DISCUSSION.

O. P. WATTS (*Communicated*): The statement that forty different chloride baths failed to show a single smooth, non-crystalline deposit, and other allusions throughout the paper to unsuccessful experiments, would seem to indicate that the experiments reported constitute but a small fraction of those carried

out. If a brief statement of the composition of every bath tried were given, it would add greatly to the value of the paper.

These remarks are not intended as a criticism, but rather to establish a rule for all papers published upon addition agents. In spite of several attempts to show that only substances of a certain kind are beneficial addition agents, so many exceptions can be taken to these attempted generalizations that the only safe rule for the experimenter to follow is to try everything. Until reliable general principles can be established it is therefore important that failures as well as successes be reported. Otherwise the man who attempts to improve still further the quality of some particular metal deposit will spend 75 percent of his time in repeating the failures of his predecessors.

In connection with the good results obtained by Prof. Mathers from solutions of cadmium fluoborate, the following extract from a laboratory report by R. C. Judd, dated December 21, 1911, may prove of interest.

The electrolyte was prepared by the electrolysis of fluoboric acid containing glycerine with a cadmium anode, until about 50 grams of metal had dissolved in 200 c.c. of electrolyte.

"Plating cadmium on copper, iron and zinc:

1. With a current density of three amperes per square decimeter for one hour.
   a. Zinc was plated on by immersion, and the deposit was worthless.
   b. Copper received a very even, hard, adherent coating, which took a good luster on polishing.
   c. Iron received a very good plate similar to the coating on copper.
2. Iron and copper were plated for forty-eight hours at three amperes per square decimeter. The deposits were adherent and solid, but there was a tendency to treeing on the edges of the cathode. The bath needs an addition agent when used for thick deposits.
3. One gram of glucose per liter was added. The above current density was used for seven days, and the deposit was still free from trees on the edges, and was very solid and adherent." This current density, twenty-eight amperes

per square foot, is unusually high for a week's deposit from a stationary solution.

Since, of those metals which can be successfully deposited electrolytically from aqueous solutions, cadmium and zinc are the only ones above iron in the electrochemical series, it was considered of interest to compare cadmium with zinc as a protective coating for iron. Strips of sheet iron electroplated with cadmium and with zinc have been exposed to the weather from December, 1912, to the present. Both sheets are perfectly protected from rusting.

F. C. MATHERS (*Communicated*): In reply to the criticism by Dr. Watts, the statement should be made that the paper describes all the essential conditions of the experiments that were tried with the forty chloride baths. The paper would have been unnecessarily lengthened by a complete description of each one of the experiments, consequently only the maximum and minimum percentages and quantities of the free acid, the ammonium chloride or other salts, the cadmium chloride and the addition substances were given. This is all that was necessary, since the baths of intermediate concentration gave results like the ones that were fully described.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

ELECTRODEPOSITION OF NICKEL.

By C. W. Bennett, H. C. Kenny and R. P. Dugliss.

A number of years ago Calhane and Gammage[1] published some very interesting facts concerning the deposition of nickel from solutions of nickel-ammonium sulphate. Although these experiments were made for the purpose of studying the impurities, such as iron, deposited with the nickel, they bring out some facts which may serve to throw light on the theory of nickel deposition.

In their work the anodes used were the commercial ones containing about 7.5 percent iron and about 92 percent nickel. The first experiment consisted in the electrolysis of the nickel solution (containing about 80 grams of nickel-ammonium sulphate per liter of water), using the nickel-iron anodes and platinum sheet cathodes. The current density was about 4 amperes per square decimeter, and the current efficiency on a one-hour run was about 88 percent, the deposit containing about 0.15 percent iron. The effect of stirring was then tried by running two cells in series, one having a stirrer which rotated 130 revolutions per minute, while the other had a stationary electrolyte. The efficiency in the two cells was practically the same, being about 90 percent. The iron in the deposit from the still solution was 0.13 percent, and that from the stirred solution was 0.36 percent. The effect of rotating the cathode was then tried by running two cells in series, the conditions being the same with the exception that one held a stationary cathode while the other had the cathode rotated 130 revolutions per minute. The efficiency of deposition was 91 percent with the stationary and 12 percent with the rotating electrode. The iron contained in the deposit was 0.11 percent for the stationary and 0.55 percent for the rotating cathode. Cathodes were used rotating 260, 519, 1,041 and 2,160 revolutions per minute, and efficiencies of 69, 65, 55 and 40

[1] Jour. Am. Chem. Soc., **29**, 1268 (1907).

percent respectively were obtained. Unless the anodes were enclosed in bags, or the cathode placed in a porous cup, the iron content of the rotating cathode was always greater than that of the stationary ones.

In view of the fact that nothing has appeared since this publication to explain the seemingly specific effect of rotation of the cathode, it was thought that an explanation should be sought with the idea of making clear some other facts found with rotating cathodes. Interest was also stimulated by the recent Symposium on Electroplating held before this Society (Vol. **23**).

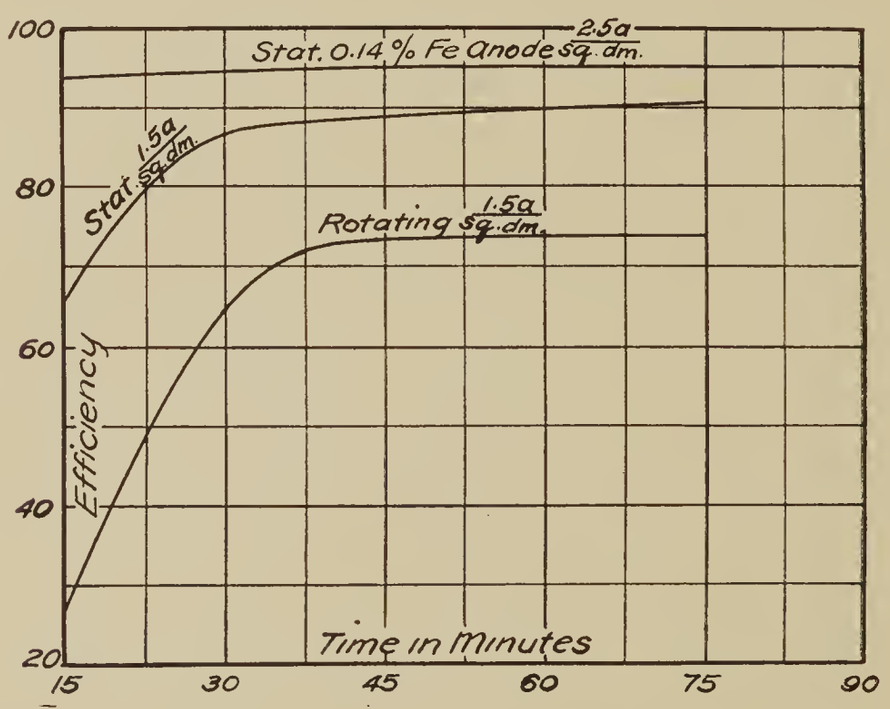


FIG. 1.

In checking up the work of Calhane and Gammage the curves of efficiency, shown above in Fig. 1, were obtained, which are plotted against time in minutes as ordinates. By running for fifteen minutes and weighing, and then continuing, the effect of time is shown very plainly. The rotating cathode shows a lower efficiency than the stationary. The solution used contained about 7 grams of crystallized nickel-ammonium sulphate and 1 gram of nickel chloride per 100 cc. of water. The anodes contained about 0.75 percent of iron. The current density was 1.5 amperes per square decimeter.

The run giving the third curve at the top of Fig. 1 was made with a solution containing 8 grams crystalline nickel-ammonium

sulphate and 1 gram nickel chloride per 100 cc. of water. The anode was 0.14 percent iron; the current density was about 3 amperes per square decimeter. Here the anode having the least iron content is in the cell which gives the highest efficiency. It was therefore thought that iron had something to do with the lowering of the efficiency.

Attempts were made to obtain pure nickel plate which contained no trace of iron, for use as anode for an efficiency test, to see if rotation would have the same effect here. It was thought possible that the voltage relation might be changed so that iron could be reduced and oxidized more easily than nickel deposited and dissolved respectively, and therefore that these reactions would go on more readily than the normal deposition of metal. The alternate oxidation and reduction of the iron, if this is the important factor, would be greatly increased by the rapid stirring and consequent mixing of the anode and cathode solutions occasioned by the rotating cathode. Attempts, however, to get a large amount of pure nickel were more or less futile, so it was decided to change the plan.

If the cathode is enclosed in a porous cup, the iron will be almost wholly kept out, so that some factors will be changed, with a probable change in the results. Consequently two cells were run in series, one with and the other without the porous cup. The solutions were free from iron, and contained, as all solutions henceforth, 8 grams of nickel-ammonium sulphate and 1 gram nickel chloride for 100 cc. of water. The chloride was added to aid the solution of the anodes (0.14 percent iron) which were used in several runs. The anodes used here, however, contained 7.6 percent iron. The current was as before. The deposits were weighed every fifteen minutes for one hour, and at longer intervals after that, giving the time-efficiency curves shown in Fig. 2.

The efficiency in the ordinary cell increases continuously, while that of the porous-cup cell increases, reaches a maximum, and then falls off. Inside of the porous cup, the cathode compartment, after 15 hours' run the solution consisted essentially of a rather concentrated solution of ammonium hydroxide, the nickel being almost wholly removed from the compartment by deposition. The cathode in the ordinary cell contained about 3.5 percent

iron, the one in the porous cup containing only 0.15 percent. After the run the solution in the ordinary cell, 400 cc., had 0.4 gram of iron present. In the porous-cup cell, inside the cup, 1.6 grams of iron were found, and 2.1 grams outside. The iron had practically all been precipitated by the ammonium hydroxide inside the porous cup. It was deposited before it reached the cathode, and hence the iron content of the cathode in the cup was low.

The fact that the cathode compartment becomes alkaline leads one at once to an important consideration, which probably throws light on the deposition of several of the metals more electropositive than hydrogen. If the measurements of the voltage

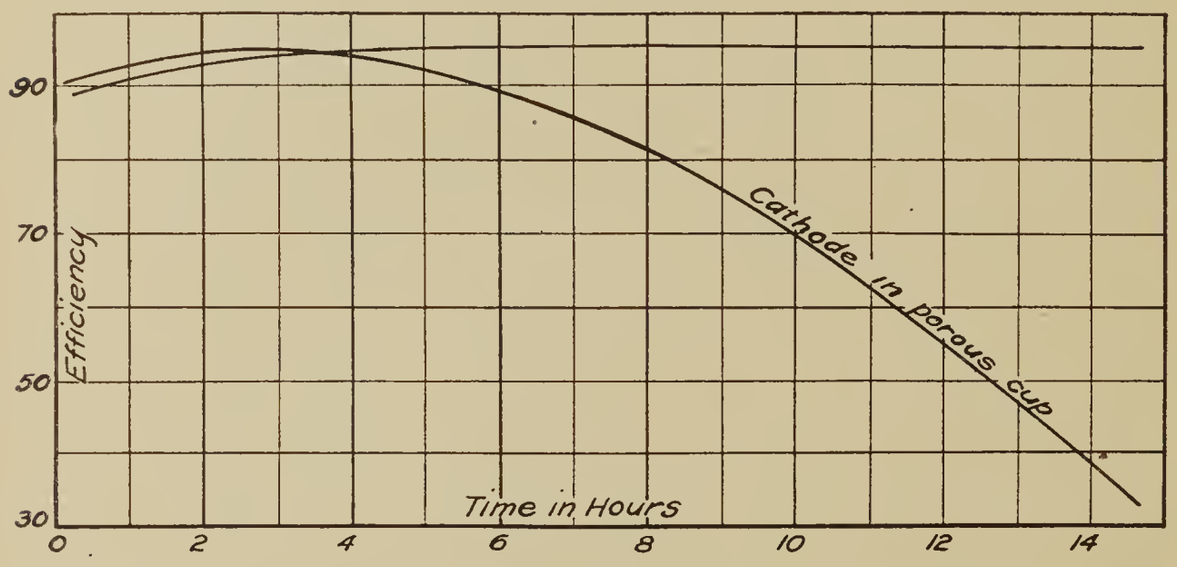


FIG. 2.

required to deposit nickel,[2] 0.228 volt, and the measurement of the over-voltage of hydrogen[3] at the surface of a nickel cathode, 0.14 to 0.21 volt, mean anything, the fact that nickel is deposited instead of hydrogen from a solution giving a slight acid reaction cannot be ascribed to the over-voltage of hydrogen, for the balance is in the other direction. It is not going too far, probably, to say that hydrogen is liberated at a nickel electrode with a smaller expenditure of energy than that required to deposit nickel. This leads directly, then, to the obvious conclusion that nickel cannot be deposited from an acid solution. When, however, the solution becomes slightly alkaline, the nickel

[2] Wilsmore: Zeit. phys. Chem., **35**, 318 (1900).

[3] Coehn: Zeit. phys. Chem., **38**, 618 (1901).
Caspari: *ibid.*, **30**, 93 (1899).

may be deposited, for the concentration of hydrogen as ion becomes practically zero in the alkaline solution. In interpreting this statement it must be borne in mind that the acidity of the solution from which the actual deposition takes place is considered, and not that of the solution out between the two electrodes. The reference is, therefore, to the film of solution which is in actual contact with the cathode.

Under this condition, suppose an electrolysis is begun with nickel-ammonium sulphate solution with nickel electrodes. The solution being neutral or slightly acid will contain the following positive ions:

$$H^{\bullet},\ Ni^{\bullet\bullet} \text{ and } NH_4^{\bullet}$$

These ions will all take part in carrying the current to the cathode. At the cathode, hydrogen will be liberated, which removal leaves an excess of hydroxyl ions which with the $NH_4^{\bullet}$ ions correspond to the ammonium hydroxide which accumulates at the cathode. No deposition of nickel can take place until the hydrogen is removed and the solution becomes alkaline. When this occurs nickel may deposit, and the efficiency of deposition will depend on the maintenance of a cathode film which is alkaline. The facts exhibited in the curves, Fig. 1, are intelligible from this viewpoint. When the electrolysis is started the efficiency is low at first, due to the fact that much of the current is used up in liberating hydrogen. When these ions are removed the cathode film is alkaline, and nickel deposits with an efficiency which gradually increases as the electrolysis proceeds, until practically a maximum value is reached, when the cathode film of solution is most favorable for the production of the best deposit.

The tendency to deposit hydrogen is greater at a platinum cathode than at a nickel cathode, on account of the over-voltage effect. It might be said, therefore, that with a platinum cathode a low efficiency would be expected, since the tendency to liberate hydrogen is greater than when a nickel cathode is used. In the former case some time is required to build up a surface of nickel, while in the case of a nickel cathode the nickel film is present from the beginning. Having the nickel surface from the beginning, the over-voltage effect would operate over a longer time

than in the case of a platinum cathode, and the tendency to deposit hydrogen would be less in the case of a nickel cathode. If the above were true the efficiency would be lower with platinum than with copper or nickel cathodes. When these were tried, practically no difference could be shown to exist, as is shown in Table I. The cells were run in series for 17 minutes.

TABLE I.

Effect of Cathodes on Efficiency of Deposition.

Cathode Material	Copper	Nickel	Platinum
Efficiency, percent . . .	95.5	96.0	95.3

These differences are well within the limit of experimental error, and show that the cathode over-voltage has nothing to do with the efficiency.

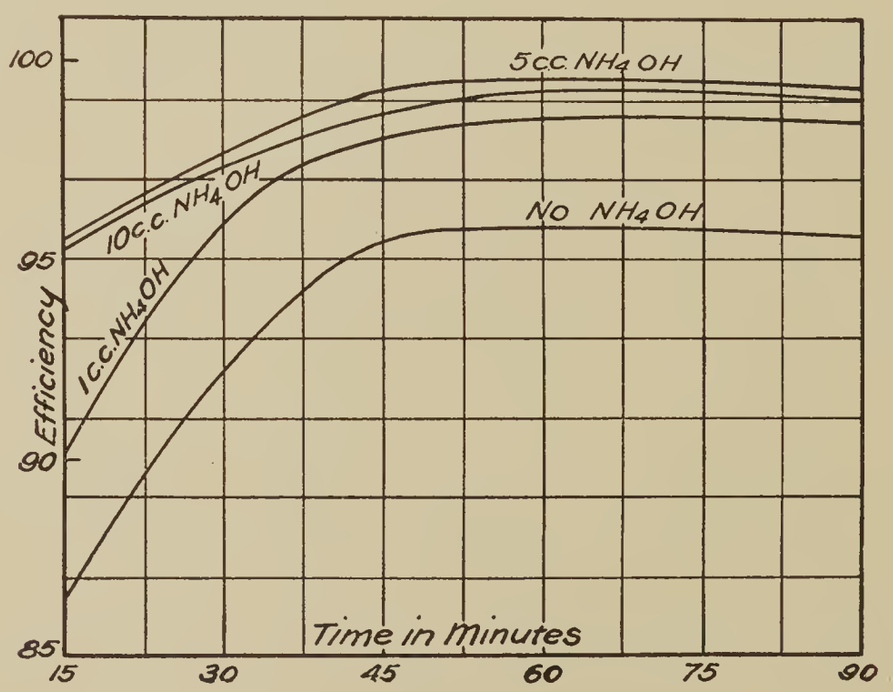


FIG. 3.

If the increase in efficiency with time is due to the accumulation of ammonium hydroxide at the cathode, this condition could be realized synthetically throughout the whole solution by adding to the solution some ammonium hydroxide. It ought to be possible to start the electrolysis with a high efficiency by adding the alkali to neutralize the acid present. Runs were therefore

made with solutions (190 cc. each) to which 2, 5 and 10 cc. of 1:10 ammonium hydroxide (Sp. Gr. 0.89) were added. With 2 cc. of material, as is shown in Fig. 3, the efficiency is increased slightly over the neutral solution, the amount of increase being very great in the cases with 5 and 10 cc. The solution containing 5 cc. of ammonium hydroxide always gave a more adherent and a better deposit. These runs are with stationary electrodes, the anodes being 0.5 percent iron, the cathode being copper, held stationary. The current density was about 1.5 amperes per square decimeter, and the cells were run in series with a coulometer as in other cases. It seems that the efficiency can be started and maintained at almost any desired point within limits by adding ammonium hydroxide. The same effect is obtained with anodes containing 7.5 percent iron, as is shown in Fig. 4.

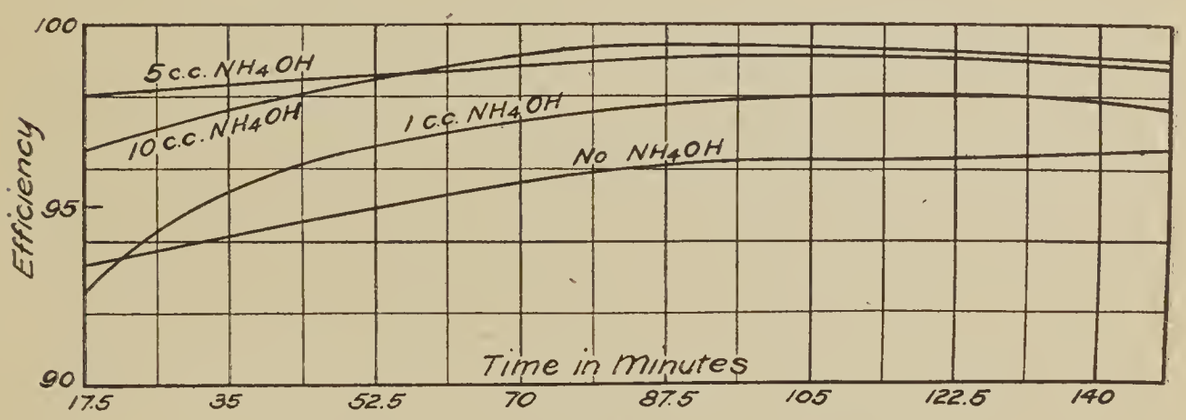


FIG. 4.

It is interesting to note the fact that iron is found in the cells after electrolysis, as is shown in Table II.

TABLE II.

Iron in Cells with Ammonium Hydroxide.

Amount of Ammonia, cc.	None	2	5	10
Iron in deposit at bottom of beaker, grams	0.0225	0.0300	0.0685	0.0442
Iron in solution, grams	0.0144	0.0092	Trace	Nil

The amount of iron in the precipitate on the bottom of the beaker increases as the concentration of alkali increases, while the amount in the solution decreases, just as it should.

The explanation of the decrease in efficiency with the rotating cathode over the stationary one becomes apparent at once. The rotation of the cathode stirs the solution and gives a very effective means of breaking up this alkaline film over the rotating part. This broken up, the efficiency is low by amounts depending on the efficiency of the removal of the ammonium hydroxide from the film. The stirring may just as well be considered as preventing impoverishment of hydrogen, which, of course, amounts to the same thing, *i. e.*, prevents the formation of an alkaline film over the cathode. The efficiency should begin lower than the stationary one, and should increase as the electrolysis proceeds, since some ammonium hydroxide is piling up in the solution.

The efficiency of removal of a surface film will depend on the speed of rotation. It may be seen, therefore, that the efficiency should decrease as the speed of rotation is increased.

Although the method of removal of this film by stirring the solution is an inefficient one, it ought to be possible to decrease the efficiency by stirring the solution without rotating the cathode. This is a necessary conclusion from the theory given above. On the other hand, Calhane and Gammage have shown that when a stirrer is rotated 130 revolutions per minute the efficiency is not greatly different from the stationary one. They have carefully avoided stirring more vigorously, even though it might easily be guessed that stirring vigorously out in the center of the solution would probably disturb the cathode film only as much as that occasioned when the cathode itself is revolved very slowly. It seemed safe to say, therefore, that if the stirring were more vigorous, the efficiency would be decreased. At any rate, since the theory requires this, the experiment had to be made.

The results for two rates of stirring will be shown. The conditions were practically the same as before: nickel anodes, 0.14 percent iron, perforated platinum sheet cathodes, solution as before (80 grams nickel ammonium sulphate and 10 grams nickel chloride per liter). The current density was about 1.5 amperes per square decimeter, and the cathodes were weighed every 15 minutes. No coulometer was used, it being desired to see the difference between a stationary solution and one which was well stirred. The containers were crystallizing dishes 12.5 cm.

in diameter, the anode being placed on one side and the cathode on the opposite side. Situated about .2 centimeters from the cathode in one cell was a cylindrical, perforated, sheet, platinum electrode about 3 centimeters in diameter and 5 centimeters long, fastened to a shank or shaft which was held in a chuck and rotated. This gave very good stirring at the surface of the cathode sheet. The rotating piece, of course, was not electrically connected, it being used only for stirring. One run was made with stirrer rotated at 420, and another at 750 revolutions per minute. The former rate of stirring gives curve A, and the

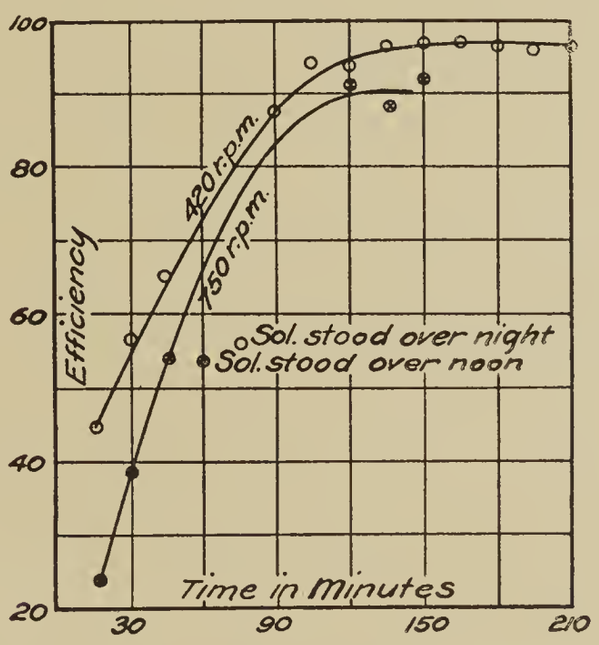


FIG. 5.

latter one curve B, Fig. 5. These curves show relative efficiencies of the cells with a still solution and that with a stirred solution. In other words, they give the efficiencies of the stirred solution as compared with the still solution, which is assumed 100 percent. From these curves the conclusion may be drawn that the efficiency of deposition decreases as the rate of stirring is increased, just as it should according to the theory just advanced.

With this a number of facts become intelligible which otherwise are weird. The curve at the top of Fig. 1, which was run at a higher current density than the other stationary curve, shows a higher efficiency because the rate of carrying in the ammonium ion is relatively greater as compared with its diffusion backward, the current density being higher. This gives conditions for the

formation of a more alkaline film where the current density is higher, and therefore the higher efficiency.

As to the behavior of iron, it may be said that if it is deposited at a lower voltage than nickel[4] it will be deposited first if it can get to the cathode. Where an ammoniacal film exists over the cathode the iron cannot get in, since it is deposited as hydrated oxide. But when the film is broken by rotation, iron may enter and be deposited. In other words, just as was found, the amount of iron in the deposit is greater with a rotating than with a stationary electrode. If iron is deposited after nickel,[5] it would be deposited when nickel is impoverished. When the electrode is rotated this impoverishment is prevented. The increase of the iron content with increasing rotation would seem to indicate that Küster's conclusion is due to some specific effect other than the voltage relations. On the other hand, it was noted that the solution became clouded in the cell with a rotating electrode. It is possible, therefore, that some of the increase could be due to mechanical deposition of the hydrated oxide which presumably causes the clouding effect.

The best deposits are obtained when the solution is alkaline at the surface of the cathode. This would mean that at the time the best deposit of nickel is being obtained it should be impossible to get iron deposited at the cathode unless it be by mechanical occlusion or deposition.

When the solution which has been electrolyzed has stood, the ammonium hydroxide necessary for good efficiency will diffuse away from the electrode and the efficiency will be less after standing—less than that obtained if the solution were worked continuously. This is shown very well in Fig. 5, where the solutions stood as noted, and it is seen from the curve that the efficiencies are very much lower than if run continuously. From the measurements as taken from the work of Calhane and Gammage, 12 percent efficiency was obtained with a rotation of 130 r. p. m. Then with 260 r. p. m., 69 percent was obtained. It appears that both must have been made in the same solution. If so, it is unfortunate that they did not try to duplicate the 130 r. p. m. run in the same solution after running the 260

[4] Toepffer: Zeit. Elektrochemie, **6**, 342 (1899).
[5] Küster: Zeit. Elektrochemie, **7**, 690 (1901).

r. p. m. one. The efficiency would probably have been about 70 percent instead of 12 percent.

CONCLUSIONS.

A good deposit of nickel may be obtained from the double sulphate if the solution at the surface of the cathode is kept alkaline.

The efficiency is dependent upon the degree of alkalinity of the cathode film.

The efficiency can be started high and maintained high by adding a definite amount of ammonium hydroxide to the solution.

The alkaline solution film at the cathode may be disturbed and the efficiency of deposition decreased by stirring the solution vigorously.

Since alkalinity is necessary for good efficiency, it is very probable that in acid solutions nickel is deposited only when impoverishment of the hydrogen ions has caused the solution to become alkaline and given the conditions under which nickel may deposit.

The iron content of a deposit formed on a rotating cathode is greater than that formed on a stationary electrode. This may be due to mechanical occlusions.

The iron content of the anode does not materially affect the efficiency.

Electrochemical Laboratory,
Cornell University.

DISCUSSION.

O. P. WATTS (*Communicated*): I congratulate the authors upon clearing up several obscure points in the electrodeposition of nickel. The necessity for alkalinity at the cathode, here pointed out, would seem to explain the oft-reiterated statement of practical platers that a good nickel deposit cannot be obtained from the single sulphate, but can from the double sulphate.

The discovery of the effect of vigorous stirring upon the current efficiency is very interesting. Several years ago I had a suspicion that there was a falling off in current efficiency at high

speeds of rotation of the cathode, but L. B. Schleeder found Faraday's law to hold for the acid copper sulphate solution up to 1,830 R. P. M. with a brass tube ¾ inch in diameter as cathode.

A. H. Frost, a student in my laboratory, on electrolyzing hydrofluoric acid for several days with a nickel anode and a carbon cathode, obtained a good white and tough deposit of nickel, although the electrolyte was still strongly acid. This fact appears to conflict with the statement on page 338 of this paper that "nickel cannot be deposited from an acid solution."

C. W. BENNETT (*Communicated*): It must be remembered that the composition of a solution in a definite place may not necessarily be the average composition. The solution between the electrodes may be acid, while the film of solution in contact with the cathode may be alkaline. It may further be questioned whether the solution of nickel sulphate or a solution of nickel fluoride can become alkaline. To make this perfectly clear it will only be necessary to make one statement, that is, that an alkaline solution is one containing an excess of hydroxyl ions. If we take an acid solution and electrolyze it, hydrogen is liberated at the cathode. This leaves the hydroxyl ion from the water in slight excess at the cathode, so that when hydrogen is separated at a more rapid rate than hydrogen ions are brought in by diffusion, convection, etc., even an acid solution may become alkaline at the surface of the cathode. An acid solution, however, will not become as strongly alkaline nor will a solution of nickel sulphate become as strongly alkaline as a solution of the double salt, on account of the fact that the hydroxyl ion concentration cannot become as great as when a base is present, as, for instance, ammonium ion or the sodium ion. This, however, is a question of degree. The deposition of nickel unquestionably takes place from a solution slightly alkaline in the case of the fluoride, made so by the excess of hydroxyl ions. This is just what we would expect, on account of the fact that the fluoride is a much weaker acid than the sulphate. In that case the fluoride would become more alkaline than the single sulphate solution, and a better deposit would be expected. These facts, instead of contradicting the statement made, must necessarily, therefore, fall in complete harmony with it.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

ELECTROLYTIC DEPOSITION OF BRASS ON A ROTATING CATHODE.

By C. W. Bennett and A. W. Davison.

In a previous paper[1] a study was made of the relation between tensile strength of electrolytic copper and speed of rotation of the cathode. The results obtained were highly satisfactory, and pointed to possibilities of wider application of the process in enhancing the physical properties and increasing the tensile strength of brass and other electrolytically deposited alloys, the unsatisfactory nature of which has long been deplored.[2] In the paper referred to above some work was reported in the copper-zinc and the copper-tin alloys, but the time at hand was inadequate for an exhaustive study of the question, and this paper is the result of further work along these lines.

It was decided at first to discard the cyanide solution because of the entirely unsatisfactory results which are obtained from it, and to search for some other solution or combination of solutions which might give a less brittle and more coherent deposit.

In order to secure the simultaneous precipitation of two metals from the same solution, the single potentials of those metals in that solution must be very close together, or else marked impoverishment must take place. Single potential measurements on solutions of the double cyanides clearly show that the curves are not necessarily coincident, but they are almost parallel and are reasonably close together. Their distance apart will depend to a certain extent on the amount of free potassium cyanide present. A brass is probably deposited from a solution of the mixed cyanides by reason of impoverishment. Reasoning from conditions in this solution, where a brass is known to deposit, to those which must obtain in any other solution from which a

[1] Bennett: Jour. Phys. Chem., **16**, 294 (1912). Tr. Am. Electrochem. Soc., **21**, 253 (1912).

[2] Field: The Electrician, **63**, 632 (1909).

brass would deposit, it is seen that the curves representing single potentials at various current densities must first of all be nearly parallel, and must also be nearly equal in magnitude. In order to determine what salts might be expected to give brass, such curves were highly desirable.

Electrochemical literature is filled with measurements of single potentials for the various metals in solutions of their salts, referred to the standard calomel electrode, but these values are all taken against stationary electrodes. With the rotating cathode, in the case of one of the metals under consideration, it has been shown[3] that marked concentration changes, accompanied by increase in potential, take place, and it was deemed desirable to measure the single potentials under conditions as near as possible to those under which precipitation would take place, in other words, with the cathode rotating at its normal speed and with full current flowing. Of course, under such conditions a brass cathode could not be realized in the measurements. Bancroft[4] has pointed out that an alloy should show the potential of its less noble phase, and Spitzer[5] has shown that electrolytic brass deviates from this but slightly. Since the measurements for the purpose at hand would be but relative, the form rather than the absolute value of the curve being desired, the fact that a brass cathode could not be maintained during the measurements is unimportant.

As previously stated, the calomel electrode is used in the majority of single potential measurements. In this instance, however, it was found difficult to keep the calomel electrode at constant distance from the cathode, for the latter was belt-driven, and its position in the cell would vary from one run to another. Fastening the calomel electrode to the cathode frame in order to secure constant separation from the cathode was impossible for mechanical reasons, hence a platinum electrode, which could be fastened to the frame of the apparatus, was substituted. This consisted of a piece of platinum wire one millimeter in diameter and twenty-five centimeters long, held firmly at a fixed distance of one centimeter from the cathode by means of a fibre strip.

The actual measurement is, therefore, the voltage drop between

[3] Bennett and Brown: Jour. Phys. Chem., **17**, 373 (1913). Trans. Amer. Electrochem. Soc., **23**, 383 (1913).

[4] Bancroft: Amer. Electrochem. Soc., 3, 297 (1903).

a platinum anode and a copper or zinc cathode respectively in the solutions used. The anode voltage will be practically constant no matter whether the solution be one of copper or of zinc salt, for the platinum absorbs practically a constant amount of oxygen. It was necessary to have the conditions such that the platinum was anode for some time before the measurement was made, so that sufficient time was allowed for the absorption of the maximum amount of oxygen. So that, while the results are probably not so accurate as if a calomel electrode had been used, they represent values which do not differ from the true ones by a large amount. It may be considered, therefore, that the potential of the platinum anode is practically constant in all the measurements, and that the change in voltage is due to other conditions, such as cathode voltage, concentration differences, and the resistance of the solution.

As in the previous work, an aluminum cathode was used, since it embodies lightness with ease of stripping off the deposit, when physical tests were to be made. In design it is similar to the one previously described,[6] although, since much smaller current densities were here used, the parts are proportionally smaller, and the water-cooled bearing was dispensed with. The cathodes proper were constructed from aluminum pipe 2.7 cm. outside diameter and 14.2 cm. long. Several of these were made to facilitate the work. At the top they were tapped to take a tapering brass plug, which securely fastened them to the remainder of the rotating parts, which consisted of the threaded plug, a steel spindle 1 cm. in diameter and 15 cm. long, an aluminum belt wheel and a brass commutator ring. The bearings, two in number, were brass, 1.5 cm. long, lubricated by vaseline supplied from ordinary grease cups. Current was taken off the commutator ring by means of two graphite brushes 1.2 cm. in diameter, held in fibre by means of coiled springs. The device was driven from a 1/8-horsepower induction motor, at the rate of 4,500 revolutions per minute, although, if desired, other speeds could be obtained by means of different sized pulleys.

Since aluminum is readily attacked by many of the solutions used, it was found necessary to protect the cathode by means of a coating of copper. This was readily applied in an acid copper

[6] Bennett: Jour. Phys. Chem., **16**, 287 (1912).

TABLE I.

Potentials of Copper in Copper Salts.

Current Density, amperes per square decimeter.	15% copper sulphate, neutral.	15% copper sulphate, 5% sulphuric acid.	15% copper sulphate, 10% sulphuric acid.	8% copper sulphate, neutral.	8% copper sulphate, 5% sulphuric acid.	8% copper sulphate, 10% sulphuric acid.	8% copper ammonium sulphate, neutral.	8% copper ammonium sulphate, 10% sulphuric acid.	8% copper ammonium chloride, neutral.	8% copper ammonium chloride + 5% hydrochloric acid.	8% copper formate, neutral.	8% copper formate + 2% formic acid.	Copper fluoride, saturated.	8% copper fluosilicate.	7% potassium cuprocyanide.
5.0	.....	.....	.....	.....	.....	.....	1.50	1.14	.....	.....	.....	.....	.....	.....	.....
4.5	.....	.....	.....	.....	.....	.....	1.30	1.08	.....	0.95	.....	.....	.....	.....	.....
4.0	.....	.....	.....	.....	.....	.....	1.22	0.98	.....	0.86	.....	.....	.....	.....	.....
3.5	.....	.....	.....	.....	.....	.....	1.17	0.92	.....	0.80	.....	.....	3.40	.....	.....
3.0	1.34	0.74	0.55	.....	.....	.....	1.12	0.88	.....	0.73	.....	.....	3.10	4.80	1.36
2.5	1.15	0.71	0.52	.....	.....	.....	0.97	0.80	0.84	0.68	.....	.....	2.72	4.40	1.55
2.0	0.97	0.64	0.49	2.25	0.58	0.58	0.85	0.75	0.77	0.63	3.40	3.30	2.47	3.80	1.45
1.5	0.84	0.57	.....	1.85	0.55	0.53	0.75	0.69	.....	.....	2.50	2.40	2.19	3.30	1.35
1.0	0.64	0.50	0.41	1.53	0.51	0.50	0.60	0.60	0.55	0.51	1.67	1.70	1.90	2.50	1.16
0.7	0.53	.....	.....	1.27	0.48	0.45	0.52	0.55	0.44	0.43	1.26	.....	.....	.....	1.03
0.5	0.44	0.40	0.37	1.03	0.45	0.43	0.45	0.52	0.40	0.38	0.98	0.96	1.57	1.48	0.92
0.3	0.30	0.35	0.35	0.81	0.43	0.42	0.35	0.49	0.35	0.34	0.70	0.62	1.35	0.95	0.83
0.1	0.25	0.28	0.31	0.61	0.40	0.39	0.26	.....	.....	.....	0.42	0.33	1.03	0.52	0.71

sulphate bath, with a current density of 25 amperes per square decimeter, the cathode being rotated. When it was desired to remove a deposit from the cathode, this layer of copper was stripped off with the brass, and afterward removed from the brass by filing or scraping.

The arrangement of the apparatus is shown in Fig. 1.

The current for electrolysis, obtained from either a 28-volt 100-ampere-hour lead battery, or from the 110-volt mains, was led in through one side of the double-throw switch directly to the

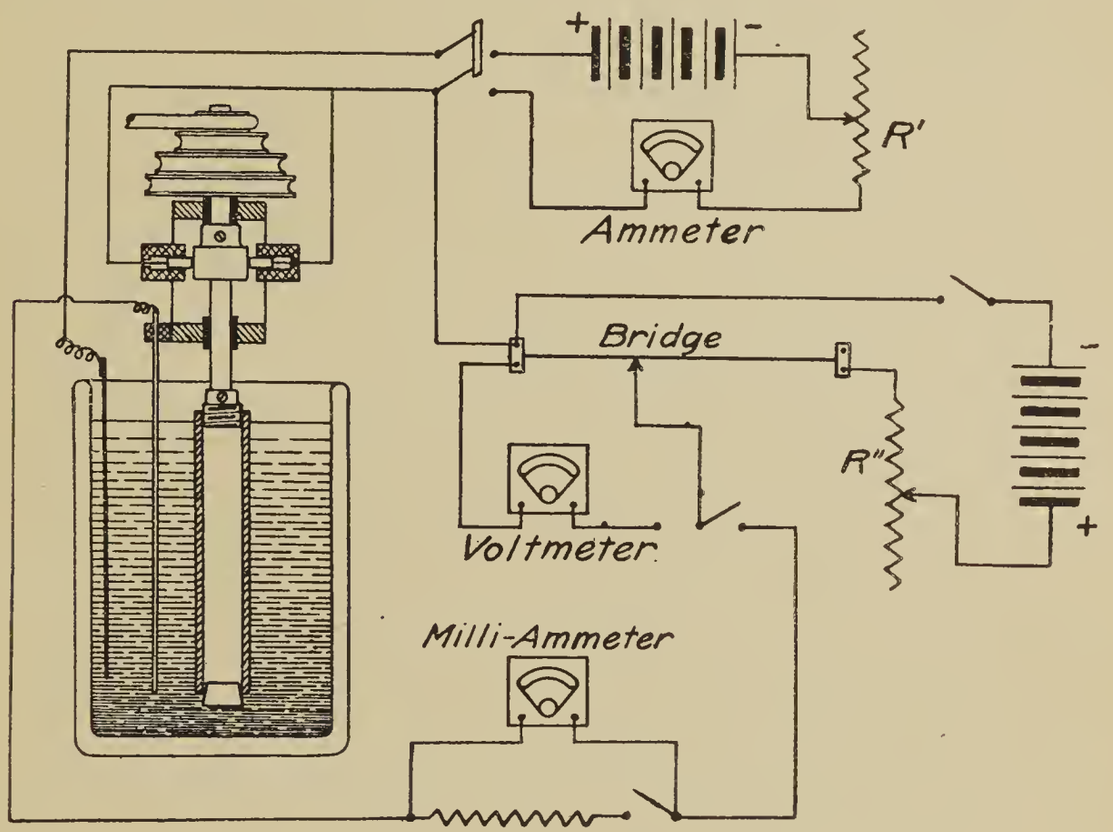


FIG. 1.

anode, and from the cathode through the other side of the double-throw switch to the ammeter and then to the adjustable resistance. The cathode was also connected to the negative end of a bridge wire, and the platinum electrode was connected through a milli-ammeter to the movable contact on the bridge. This bridge was in the circuit of a 6-volt Edison set, so that the single potentials were balanced against the drop across the bridge, and this drop measured by throwing the movable contact into circuit with a high-resistance voltmeter by means of a double-throw switch. Since only relative values that would be consistent among themselves were required, the objection that the voltmeter does not

TABLE II.

Potentials of Zinc in Zinc Salts.

Current density in amperes per square decimeter.	8% zinc sulphate, neutral.	8% zinc ammonium chloride, neutral.	8% zinc ammonium chloride + 1% hydrochloric acid.	8% zinc ammonium chloride + 2% hydrochloric acid.	8% zinc ammonium sulphate, neutral.	8% zinc ammonium sulphate + 1% sulphuric acid.	8% zinc ammonium sulphate + 2% sulphuric acid.	4% potassium zincate.	4% potassium zincate + 2% potassium hydroxide.	Zinc fluoride, saturated.	8% zinc benzene sulphonate.	8% zinc fluosilicate.	5.25% potassium zinco-cyanide.
4.0	.....	.....	.....	.....	.....	2.72	2.49	.....	.....	4.20	.....	.....	.....
3.5	3.50	.....	.....	.....	2.95	2.43	2.38	2.35	.....	4.00	4.50	.....	.....
3.0	3.20	.....	.....	.....	2.57	2.27	2.08	2.11	2.32	3.80	4.20	.....	.....
2.5	2.93	.....	.....	.....	2.43	2.03	2.02	1.93	2.06	3.60	3.80	4.80	.....
2.0	2.55	1.95	1.53	1.39	2.30	1.95	1.88	1.81	1.91	3.40	3.50	4.30	1.76
1.5	2.20	1.57	1.34	1.31	2.12	1.83	1.69	1.73	1.81	3.10	3.20	3.70	1.68
1.0	1.90	1.48	1.26	1.26	1.75	1.71	1.51	1.66	1.68	2.75	2.85	2.90	1.64
0.7	1.67	1.45	1.20	1.18	1.60	1.56	1.36	1.58	1.58	.....	.....	.....	1.53
0.5	1.51	1.39	1.16	1.15	1.48	1.47	1.26	1.55	1.52	2.33	2.41	1.85	1.41
0.3	1.33	1.30	1.12	1.10	1.41	1.40	1.18	1.51	1.47	2.06	2.29	1.39	.....
0.1	1.23	1.22	.....	.....	1.28	1.15	.....	1.41	1.39	1.68	2.11	1.20	.....

measure the actual drop at the instant of balancing is overcome. The milliammeter was used in place of a galvanometer, because commutation troubles at the cathode with high current densities would cause the galvanometer to go off the scale. Some difficulty was encountered at the commutator, due to thermo-currents and consequent electromotive forces, but, by allowing the cathode to run until the maximum temperature was reached at the commutator each time before measurements were made, that was eliminated.

The cell consisted of a 1.5-liter glazed porcelain battery jar, and the anodes were of uniform size, 12.5 x 5 x 0.1 cm. The runs were made at 25° C.

The potentials for copper solutions are given in Table I; for zinc solutions in Table II.

With current flowing the potentials represent several factors—the potential of the cell oxygen-solution-copper or oxygen-solution-zinc, the drop across the commutator and the drop across the solution. The last named could have been eliminated only by placing the platinum wire at an infinitesimal distance from the cathode, where the strong agitation would have immediately bent it away.

Cupric-ammonium chloride cannot be used in plating baths because of the formation of a heavy flocculent precipitate, which is doubtless cuprous chloride. Single potentials of this salt were measured, however, and the curve was plotted, in order to give some idea of the potential. The deposit in the case of zinc-ammonium chloride was worthless, and the same is true of the one obtained from neutral copper formate.

With copper benzene sulphonate the deposit was of a doubtful value, and potential measurements were impossible because the platinum wire at once became covered with a black layer of copper when it was placed in the solution. In all the other cases recorded, good deposits of the metal were obtained, and it was assumed that they were capable of further exploitation.

In plotting these curves representing single potential against current density, for the sake of simplicity the zinc salts were plotted on one sheet and the copper ones upon a separate one, Figs. 2 and 3.

A consideration of the curves shows that the pairs of similar form and of comparable magnitude are the following:

1. Copper sulphate and zinc sulphate.
2. Copper fluosilicate and zinc benzene sulphonate.
3. Copper benzene sulphonate and zinc sulphate.
4. Copper fluosilicate and zinc fluosilicate.
5. Copper fluoride and zinc fluoride.
6. Copper fluoride and zinc sulphate.
7. Copper ammonium sulphate and zinc ammonium sulphate.

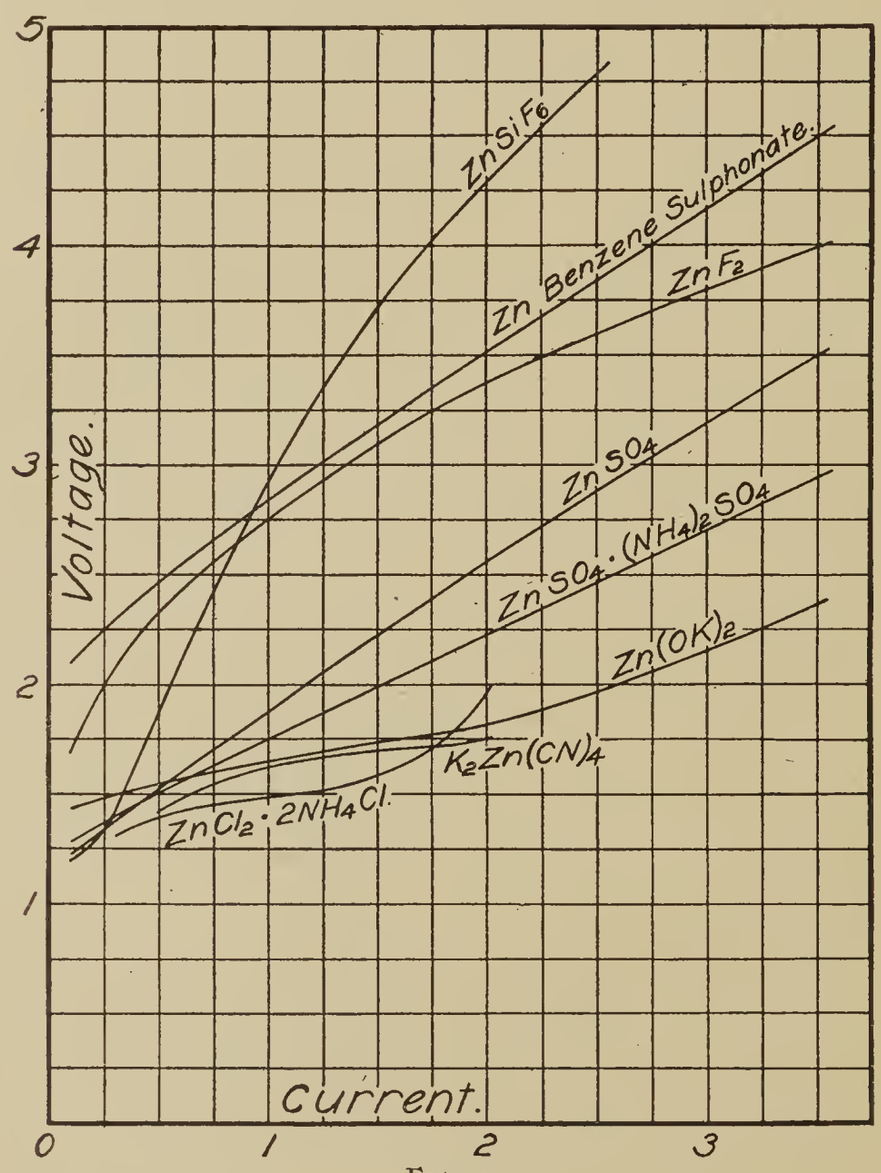


FIG. 2.

The results of the individual runs are as follows:

It was certainly not to be expected that a brass could be deposited from a solution of the mixed sulphates, since it is the one employed in the quantitative separation of these metals in

the determination of copper. A good deposit cannot be obtained from neutral solution; acidification introduces an ion whose potential is between those of the two metals, and hence simultaneous deposition of the metals is impossible.[7]

Above a current density of 1 ampere per sq. dm. the curves for copper fluosilicate and zinc benzene sulphonate come the nearest of all to coincidence, the potentials being but a small fraction of a volt apart. But when one considers that a solution

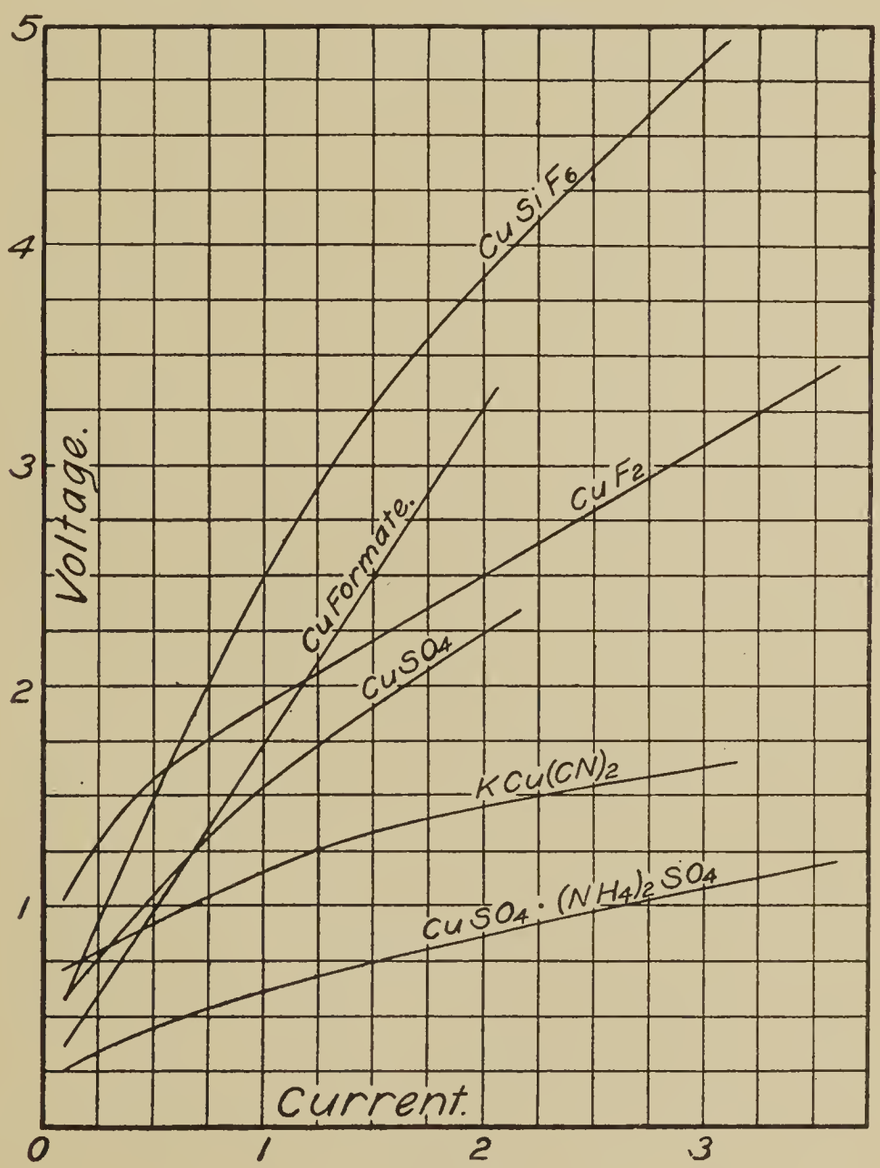


FIG. 3.

of the two salts will contain molecules of the four compounds, copper fluosilicate, copper benzene sulphonate, zinc fluosilicate and zinc benzene sulphonate, it is quite apparent that the metal which will be precipitated will be the one having the salt of the lowest

[7] Field: The Electrician, 63, 632 (1909).

single potential—in this case copper from benzene sulphonate. Experiment showed that under all conditions of current density and concentration, except where the copper concentration was slight and the zinc deposit bad, copper was deposited or else was accompanied by a worthless deposit of zinc.

Copper benzene sulphonate and zinc sulphate can be dismissed with very little comment, for copper sulphate is formed in the bath, and, since it possesses a much lower potential than any of the other salts present, copper alone is deposited.

With copper and zinc fluosilicates the potential of zinc is uniformly higher than that of copper, although the difference is not so great as in many other instances. It was thought that, by starting with a zinc solution and running the cell with a copper anode, a point would finally be reached where the concentration of both salts would be right for the deposition of brass. Should such a point be reached, a brass anode of the desired composition could be substituted, and, barring difficulties of corrosion, the brass should continue to deposit. Accordingly a solution containing 8 percent zinc fluosilicate was prepared, and electrolyzed with an anode and cathode current density of 5 amperes per sq. dm., with a copper anode, until the copper content was high enough to give copper at the cathode. This deposit was worthless, due, it was thought, to too high a current density. A zinc anode was then substituted, and the cell run with a current density of 1 ampere per sq. dm. until zinc began to deposit again. This procedure was carried out repeatedly, with current densities of from 0.1 to 10 amperes per sq. dm., but in no case was a brass observed. The deposit, too, was worthless, tending to grow out in flaky masses and to fall off. The zinc would be a dirty black, and the copper a sickly-looking red. Addition of 12 percent free fluosilicic acid did not improve the deposit.

Just at the point where the cell seemed to change from depositing zinc to copper a brass anode was put in, and electrolysis continued with a current density of 1 ampere per sq. dm. for three hours in order to determine under what conditions the metals were being deposited at the concentration of solution. A black incoherent deposit was found on the lower half of the cathode, and a bad copper deposit above this where the air was stirred down by the cathode. After the run was stopped a mass

of finely divided zinc settled to the bottom of the cell. This peculiar segregation of the deposit was undoubtedly due to the fact that bad zinc and copper were being deposited together over the cathode, but that the color of zinc was predominant. At the top, where surging of air bubbles took place, the zinc was partly oxidized, and knocked off, leaving the copper on the cathode. The actual amount of copper in the solution when that metal would deposit was always small, because rapid agitation prevented excessive impoverishment.

A few experiments made on this same solution with stationary electrodes failed to show any deposit of brass. Much smaller current densities were used, ranging from 0.1 to 1.0 ampere per sq. dm. The conditions of deposition were very much the same as with the rotating cathode, except that a great deal more copper was required in the solution before that metal would precipitate in any large percent. This was, no doubt, occasioned by impoverishment of copper at the cathode, which permitted slimy zinc to deposit.

In this case the metals are too far apart in potential, for when the composition of the bath is right for their precipitation in the ratio required for brass, none results.

The curves for the mixed fluorides certainly do not indicate that a brass can be deposited from these solutions, and tests similar to those of the preceding instances failed to give any at all.

Copper fluoride and zinc sulphate seem to give curves that are quite similar in form, and a number of experiments were made on these solutions. A brass could not be deposited at any current density, under any conditions of concentration. This case is entirely analogous to the one of copper fluosilicate and zinc benzene sulphonate in that double decomposition results in the formation of copper sulphate, copper fluoride, zinc sulphate and zinc fluoride, and when these salts are present in the bath together copper alone is deposited from the sulphate.

The curves for the double ammonium sulphates are so far apart that results could not be obtained from them.

In addition to those salts for which single potentials were measured, a few runs were made on molecular solutions of the mixed chlorides, using 5 percent sodium chloride to insure quantitative solution at the anode. Starting with a zinc solution,

and using a copper anode, the latter metal would dissolve in the zinc chloride as cuprous chloride. Various concentrations of copper up to the point where cuprous chloride would slime at the anode were tried, but no brass was obtained, although it was possible to get the zinc and copper precipitating at the same time under conditions which were not noted, because the copper would not stick to the cathode, but was thrown around in the solution, settling out after the run was stopped.

Hydrolysis of the zinc, with precipitation of white zinc hydroxide, caused trouble to a great extent in this solution also.

The general nature of the deposit indicated that perhaps the solution was too concentrated, and another run was made, using a normal solution, 2 percent sodium chloride and 5 percent hydrochloric acid added to drive back hydrolysis of the zinc. Careful variation of current density and metal ratio failed to show any brass deposit, the character of the deposit being much the same as for the more concentrated solution.

A general survey of the more common salts and those, cyanides excepted, which give good and indifferent deposits from single solutions therefore results in failure to find a satisfactory solution for depositing brass. Brasses obtained from the cyanide solutions are known to be unsatisfactory from the physical standpoint.[8] It was therefore deemed advisable to investigate the causes of this undesirable property and to remedy it if possible. A number of runs was therefore made with cyanide solutions, the results of which follow.

In preparing the solutions, copper or zinc sulphate in solution was treated with an amount of potassium cyanide equivalent for the formation of the simple single cyanide, and the precipitate filtered out and washed free from sulphates. It was then dissolved hot by treatment with sufficient potassium cyanide solution to give the double cyanide plus one molecule of free potassium cyanide, that amount being necessary in order to secure quantitative solution of the anode. There is, however, the disadvantage that strong hydrogen evolution takes place with increasing cyanide concentration.[9]

By preparing solutions of both potassium cuprocyanide and

[8] Bennett: Jour. Phys. Chem., **16**, 294 (1912). Field: Electrician, *loc. cit.*

[9] Field: *loc. cit.* Spitzer: *loc. cit.*

potassium zinc cyanide in this manner, and mixing them, it was possible to vary the metal content very easily. The method of "working one metal into the bath," much used by practical platers, was quite frequently resorted to also. When a solution was depositing a brass satisfactorily, analyses were made for copper, zinc and free potassium cyanide. The copper was determined by the usual electrolytic method of converting to sulphate by "fuming down" 25 cubic centimeters of sample with 10 cubic centimeters of concentrated sulphuric acid, diluting to 500 cubic centimeters, neutralizing with ammonia, then adding 10 cubic centimeters of sulphuric acid and electrolyzing with platinum flag anodes and rotating copper cathodes. Zinc was then determined from this same solution by the pyrophosphate method as modified by Findlay and Cummeley.[10] The nickel method of Lundell,[11] which gives free alkali cyanides in the presence of copper and zinc, was employed in determining free potassium cyanide.

The brasses were analyzed by the same scheme, after having been dissolved in nitric acid.

For carbon and hydrogen in the brass an ordinary electric combustion oven, heated to 900 degrees, was employed, using for the oxidizing agent air previously bubbled through 2:1 potassium hydroxide, and concentrated sulphuric acid. Water from oxidation of hydrogen was collected in concentrated sulphuric acid, and carbon dioxide in 2:1 potassium hydroxide followed by concentrated sulphuric acid.

The samples were also polished, etched with 1:3 ammonia, and photomicrographs were taken, to get at their structure and general appearance.

The procedure in the first run was to start with a molecular solution of copper double cyanide containing one molecule free potassium cyanide and to run with a zinc anode until brass appeared at the cathode. The current density was 3 amperes per sq. dm. When the cathode was first examined the deposit seemed to be nearly all zinc, showing that the concentration of zinc necessary to give a brass had been exceeded; hence a copper anode was substituted and the deposit watched more closely until

[10] Jour. Chem. Soc., **103**, 1104 (1913).

[11] Trans. Am. Electrochem. Soc., **25**, 369 (1914).

the brass reappeared. Then a brass anode, copper 70 percent, zinc 30 percent, was put in, and the cell run until a deposit 1 mm. in thickness had formed on the cathode. This brass was very brittle, non-homogeneous and extremely hard; hence no analyses were made of it or of the solution.

The second run, 25 hours with a current density of 3 amperes per sq. dm., was discontinued because the brass proved to be extremely brittle.

The cyanide content in the third run was quite high, probably above 50 grams per liter, so that appreciable solution of the

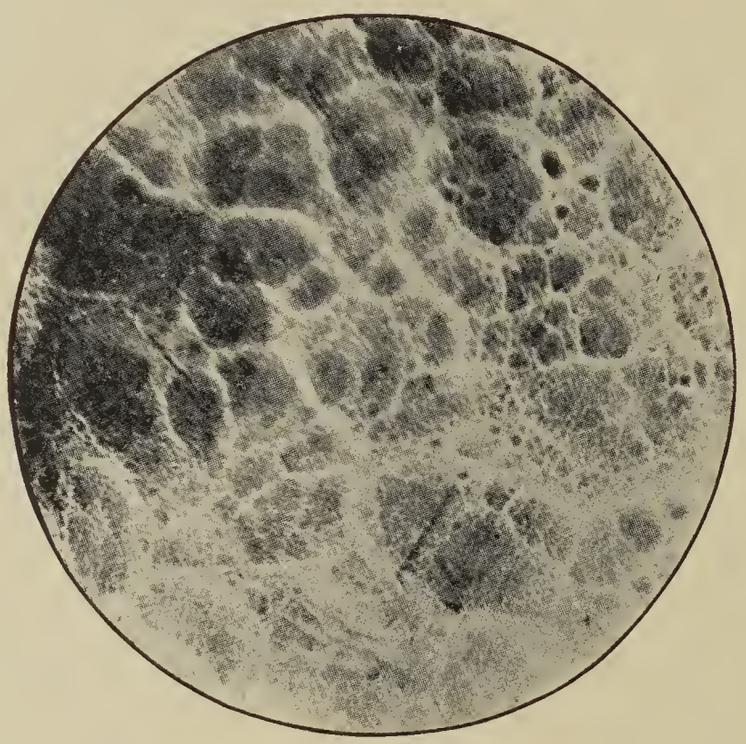


FIG. 4.

cathode took place, and holes developed in the copper coating of the cathode, which permitted the solution to attack the aluminum.

The fourth run was made with a current density of 3 amperes per sq. dm. for 58 hours; 95 grams of brass were deposited, with an efficiency of 53 percent. The metal contained 71.5 percent of copper and 27.7 percent zinc, 0.07 percent carbon and 36 volumes of hydrogen. The carbon may come from colloidal carbon precipitated with the metal, from occluded cyanogen or from potassium cyanide mechanically enclosed in the particles. The last possibility is doubtless the truth, because the odor of

hydrocyanic acid was very pronounced when the sample was dissolved. If the carbon be calculated in terms of potassium cyanide, it gives a value of 0.28 percent, and the analysis totals up 99.65 percent. The composition of the bath was:

	Grams per Liter
Copper	50.8
Zinc	7.1
Free potassium cyanide	30.0

The metal was extremely hard and very brittle. It resembled in appearance and color ordinary cast brass of the same composi-

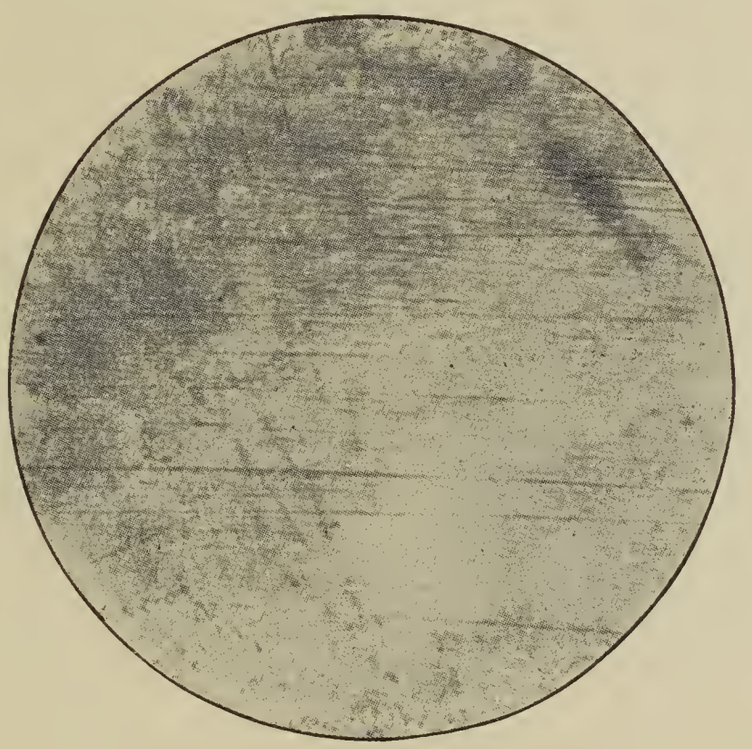


FIG. 5.

tion. The photomicrograph, Fig. 4, shows a very peculiar construction, definite crystal form evidently being entirely lacking. The structure was wart-like, with small canals running in every direction throughout the mass. These may be attributed to the impurities in the metal.

A sample, Fig. 5, was boiled for two hours in tenth normal potassium hydroxide[12] for the purpose of removing hydrogen. This was much more homogeneous, the canals were almost entirely removed, and the crystals were much smaller. The tensile strength was increased somewhat by this treatment, but not enough to warrant physical tests. Annealing at this point would

[12] Johnson: Proc. Roy. Soc., 23, 174 (1875).

have undoubtedly increased the tensile strengths immensely, but that procedure is outside the province of this paper.

In order to cut down the amount of hydrogen present in the deposit a higher temperature was desirable; hence the next run was carried on at 80 degrees, the cell being heated by means of an electric hot plate. Water was added from time to time in order to keep the volume of the solution constant. The preceding solution was used, after having had its metal content adjusted by alternately running with zinc and with copper electrodes until the brass was of the desired composition. The current density could be raised to 4.7 amperes at this temperature, and the deposit was obtained with higher efficiency. The resulting brass was extremely hard and very brittle, but less brittle than the preceding samples. The photomicrograph, Fig. 6, shows that the

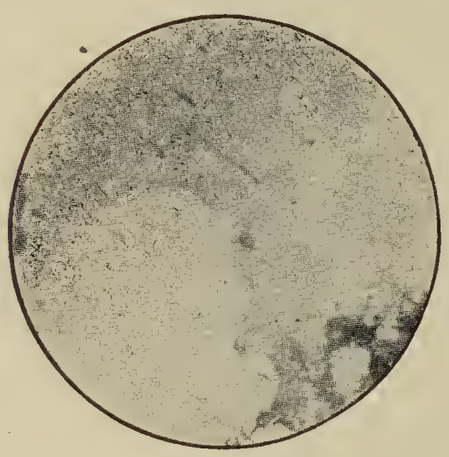


FIG. 6.

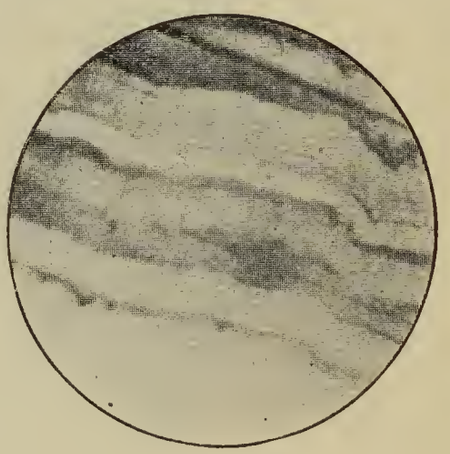


FIG. 7.

deposit is more compact, but it was not satisfactory. The hydrogen in the sample ran 10.2 volumes, and the carbon 0.08 percent. Thus heating the bath lowers the amount of hydrogen, but does not tend to change the amount of carbon to any marked degree. The metal content of the deposit was: Copper 70.4 percent, zinc 28.7 percent. A photomicrograph, Fig. 7, taken on a plane perpendicular to the axis of the cathode showed marked striations throughout the deposit, caused by variations in the composition of the bath, due to evaporation and subsequent replacement of water. Temperature variations of plus or minus 5 degrees also took place, and that would change the metal ratio of the deposit. Removal of the cathode for inspection may also have caused faults in the deposit.

In order to ascertain to some extent the effect of concentration

in the next run, the concentration of the components of the bath was reduced, and, after the usual thickness of brass was deposited, analysis showed the following composition of the bath:

	Grams per Liter
Copper	25.8
Zinc	3.4
Free potassium cyanide	36.0

This is what one would predict in a cell where rapid circulation of the electrolyte is being maintained, since increasing the amount of free cyanide increases the potential of copper more than that of zinc,[13] and as the potentials become farther and farther apart the concentration of the more noble metal must decrease faster than that of the less noble one. The presence of carbon and cyanogen in the samples leads to the supposition that these impurities come from the free potassium cyanide in the solution. The presence of this substance serves two purposes: First, it insures quantitative solution of the anode, and, second, it brings the decomposition potentials of copper and zinc nearer together. These two results can be accomplished in a slightly different way, and it was decided to eliminate the free cyanide to see if some of the bad effects could not be eliminated. The solution of the anode can be forced by the addition of a small amount of a soluble chloride or a sulphate—for instance, sodium chloride or sodium sulphate. Consequently the decomposition potentials of the two metals may be more or less taken care of by concentration differences, that is, the concentration of the one salt can be made very low, while the concentration of the other one is relatively high. It was therefore decided to make an experiment with practically no free cyanide in the solution, in which sodium chloride was added to ensure the solution of the anode.

With the free potassium cyanide content reduced to a minimum, and with 1 percent sodium chloride in the solution, a bath, whose metal composition was not determined, gives a brass at current densities as high as 5 amperes per sq. dm., when run at 25 degrees, but the deposit is just as brittle as before. If the temperature be raised to 80 degrees, cuprous chloride gradually forms, and the deposit consists largely of slimy zinc.

When 1 percent sodium sulphate is added to a solution of the

[13] Thompson: *loc. cit.* Spitzer: *loc. cit.*

double cyanides containing no free cyanide, the anode dissolves satisfactorily, but the deposit is quite analogous to those obtained in the previous instances. Analysis of a bath which had been depositing brass for some time showed approximately 30 grams of copper and 20 grams of zinc per liter. After this cell had been running for some hours the deposit at the top of the cathode became high in zinc, while that lower down was normal. This was caused by oxidation, for when the cell was run with illuminating gas above the solution, brass was deposited throughout the entire immersed area.

The usual brass plating that is applied to objects in a stationary bath or by the "barrel method" conforms to the trade requirements of hardness and beauty, so that it is an admirable protecting agent. It is possible to give it a very high polish, but its hardness must not be confused with true tensile strength. If one allows a stationary deposit to build up until a thickness of several millimeters be attained, and then strips it off the cathode, it is found that it can be broken with very little exertion, and it seems that the physical structure and properties of such a deposit are very analogous to those of the brasses described in this paper, and that the very low tensile strengths are due to the same occluded impurities. Some runs in stationary baths show that a good brass may be deposited from a solution containing 130 grams potassium copper cyanide, 44 grams potassium zinc cyanide and 65 grams of free potassium cyanide per liter. This corresponds to an approximate metal content of copper 53 grams and zinc 12 grams per liter. It is interesting to note the difference in the metal ratio in a bath which will give a good brass in a stationary solution and that in a bath whose cathode is rotating at the rate of 4,500 revolutions per minute. The free cyanide content is practically the same in both cases.

	Grams per Liter	
	Stationary	Rotating
Copper	53.0	50.8
Zinc	11.5	7.1
Ratio: copper to zinc	1 : 0.22	1 : 0.14

This is accounted for by the fact that in the presence of free cyanide the electromotive force of copper is greater than that of zinc,[14] and therefore zinc tends to deposit first. In the sta-

[14] Thompson: Proc. Roy. Soc. (London), **42**, 387 (1887).

tionary cell impoverishment of zinc at the cathode brings the content of that metal down to a value at which copper and zinc can be deposited simultaneously in the proportion required. The zinc content at the cathode is lower than that out in the body of the solution. With the rotating electrode, where impoverishment is prevented by rapid stirring, the concentration at the cathode is practically the same as that throughout the whole solution. Consequently the ratio of zinc to copper is necessarily lower than in the former case.

If this be true there must be some limiting speed of the cathode, above which brass will not deposit from a solution that will give it in an unstirred bath. To test this the solution just described for use in an unstirred bath was used, and a current density of 1 ampere per sq. dm. maintained, while the speed of the cathode was varied. The results were as follows:

Speed of Cathode	Character of Deposit
0	The usual stationary brass plating.
500	No apparent change.
1000	Still no apparent change.
1500	The brass is still excellent.
2000	Yellow brass depositing.
2500	Deposit extremely high in zinc.

Thus the speed 2,000 gives to the solution sufficient agitation to practically nullify impoverishment of zinc for this particular current density, 1 ampere per sq. dm., and the purity of the zinc deposit becomes nearer and nearer 100 percent as the speed of rotation is increased above that point.

Conclusions.

1. Measurements have been made of the voltages required to deposit copper and zinc from a number of solutions with rotating cathodes, the voltages being measured against an oxygen electrode.

2. Those solutions giving similar curves have been studied with a view to obtaining a good deposit of brass.

3. A brass was not obtained in any case, except from the cyanide solution.

4. The deposition of brass from cyanide solution is probably due to two factors: First, the tendency for the potentials of

copper and zinc to become the same in the cyanide solution, and, second, the increase in the potential of the more noble metal by impoverishment.

5. The latter factor is practically eliminated by using the rapidly rotating cathode.

6. A *satisfactory* brass has not been deposited from the cyanide solution on the rotating cathode.

7. The brittleness of the alloy is probably due to occluded impurities. Hydrogen was removed from the alloy by heating in alkali.

8. The disturbing factor probably arises from the cyanide itself, which it seems impossible to eliminate.

9. The effect of impoverishment has been shown by showing that a brass may be obtained up to a limiting speed of rotation of the cathode, beyond which zinc alone is deposited.

10. The metal ratio of copper to zinc in solutions for the deposition of a brass varies not only with variations of free cyanide, but also with the rate of rotation of the cathode.

Electrochemical Laboratory,
Cornell University.

DISCUSSION.

F. A. LIDBURY: In relation to these electrolytic papers, it would be a very desirable practice if all authors expressed the strength of the solutions in grams per liter, and also gave the density of each solution. It is difficult, when looking up work on an electrolytic problem, to get complete information as to the nature of the solution used. Of course, there is almost always sufficient data given to permit duplication of the work, but it defines the solution better to give its composition in grams per liter and to add its density. In technical work it is not only the composition of the solution that is important, but also the volumetric relations. It is very easy after making a series of solutions for work of this kind to determine the density or volume relations in some way, even if it is not done with the greatest accuracy;

but when it is desired to make use of the results in papers of this kind, where the volumetric as well as the composition relations are required, it is often necessary to go back over the work, make up the solutions and a series of calculations in order to get information which with little trouble could be given by the author.

I feel very strongly about this matter, and think that it is something which the Publication Committee might take up, making the printing of the papers conditional on so expressing these things.

G. A. ROUSH: I think that it is also desirable, in reporting on experiments of this kind, to indicate unfavorable results as well as favorable results. It helps a man but little to take up a paper of this kind, and find only favorable results, if he has no personal knowledge of the subject in question. It is not necessary to go into detail in the description of the unfavorable experiments, but simply to indicate the nature of those experiments which gave unfavorable results, and thus save the time and trouble of going over these things a second time, unless the second experimenter has reason to doubt the accuracy of the results as recorded.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

A NEW METHOD FOR THE DETERMINATION OF FREE CYANIDE IN ELECTROPLATING SOLUTIONS

By Gustav E. F. Lundell.

The existing methods for the above determination are unsatisfactory. The new method is not perfect but it is superior to the older methods because it gives more accurate free cyanide values and is less subject to interfering substances.

Briefly stated, the new method consists in titrating an ammoniacal cyanide solution containing a small quantity of dimethyl glyoxime, with the standard nickel-ammonium sulphate solution until a permanent red precipitate is produced. The reactions involved are expressed by the equations:

$$NiSO_4 + 4KCN = K_2Ni(CN)_4 + K_2SO_4$$
$$NiSO_4 + 2C_4H_8N_2O_2 = Ni(C_4H_7N_2O_2)_2 + H_2SO_4$$
$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + H_2O$$

No permanent red precipitate of nickel dimethyl glyoxime is formed until all of the free cyanide has been used up in the reaction expressed by the first equation. Free sulphuric acid hinders the precipitation of nickel dimethyl glyoxime, hence the ammoniacal cyanide solution.

Two solutions are required:

1. *A Standard Nickel Solution.* This is prepared by dissolving 15.3 grams of nickel-ammonium sulphate in water containing 5 c.c. concentrated sulphuric acid, diluting to one liter and standardizing as directed below.

2. *A Dimethyl Glyoxime Solution.* This is prepared by dissolving 8.9 grams of dimethyl glyoxime in one liter of 95 percent alcohol.

Standardization of the Nickel Solution.

Unless the percentage purity of the nickel-ammonium sulphate is known, the prepared nickel solution must be standardized as

follows: 25 cc. portions are diluted with distilled water to 200 cc., treated with 0.2 gram tartaric acid and heated to boiling. Glyoxime solution sufficient to precipitate all the nickel is now added. If the glyoxime solution has been made up according to the formula above, 30 cc. should be sufficient. After the addition of the glyoxime, the solution is made slightly alkaline with ammonia, boiled for two minutes and then set aside to digest for one-half hour. The precipitate is caught on a tared Gooch crucible, washed with 200 cc. of hot water, dried for 45 minutes at 120° C, and weighed. The weighed precipitate contains 20.31 percent nickel. From the equations given above the potassium cyanide titre of the solution can readily be calculated. If a chemically pure potassium cyanide is at hand, the above titre can be determined directly by titrating weighed portions as directed in the "Method of Analysis" given below.

Method of Analysis.

A measured volume of the electroplating solution is diluted to 100 cc., treated with 1 cc. of ammonium hydroxide, 1 cc. of the dimethyl glyoxime solution and then titrated to a permanent red precipitate with the standard nickel-ammonium sulphate solution. The color play toward the end of the reaction resembles that seen in the titration of an alkaline methyl orange solution with an acid solution. For the sake of accuracy, and also convenience, the volume of electroplating solution taken should contain from 0.2 to 0.5 gram of free cyanide.

Table I gives an idea of the accuracy of the method:

TABLE I.

Sample	Per cent. KCN found by:—		
	Gravimetric Method*	Nickel-Ammonium Sulphate Method	Liebig's Method
1. KCN No. 1 . . .	94.84	94.4	95.8
2. KCN No. 2 . . .	94.58	94.00	95.21
3. NaCN No. 3 . .	80.92	80.61	81.59

* Corrected for Chlorides.

Table II shows the freedom of the method from possible interfering substances:

TABLE II.

Volume of .1% KCN Solution used	Foreign Substance added	Volume of Nickel-Ammonium Sulphate Solution required
50 cc.	None	49.45 cc.
50 cc.	1 gram KCNO	49.45 cc.
50 cc.	1 gram KCNS	49.46 cc.
50 cc.	1 gram KCNS	49.41 cc.
50 cc.	10 grams K_2CO_3	49.55 cc.
50 cc.	20 grams K_2CO_3	49.62 cc.
50 cc.	1 gram K_2SO_4	49.43 cc.
50 cc.	1 gram NH_4CL	49.42 cc.
50 cc.	1 gram NaCl	49.47 cc.
50 cc.	1 gram NH_4NO_3	49.39 cc.
50 cc.	1 gram $NaHCO_3$	49.42 cc.
50 cc.	1 gram KOH	49.5 cc.
50 cc.	1 gram K_4FeCN_6	50.75 cc.

Table III proves that the new method gives only the free cyanide in silver cyanide solutions:

TABLE III.

KCN added to a solution containing only $KAg(CN)_2$	Free KCN found by the new method
0.0403 gram	0.0400 gram
0.0805 gram	0.0804 gram
0.1208 gram	0.1205 gram

Table IV indicates that the new method gives only the free cyanide in copper cyanide solutions:

TABLE IV.

KCN added to a solution containing only $KCu(CN)_2$	Free KCN found by the new method
0.0383 gram	0.0380 gram
0.0766 gram	0.0760 gram
0.1915 gram	0.1906 gram

Table V shows that the new method gives more than the free cyanide in zinc cyanide solutions:

TABLE V.

KCN present as $K_2Zn(CN)_4$	KCN added	KCN found
0.0642 gram	0.4161 gram	0.4702 gram
0.1283 gram	0.3520 gram	0.4612 gram
0.3208 gram	0.1595 gram	0.4249 gram

The nickel-ammonium solution reacts to some extent with $K_2Zn(CN)_4$, the reaction ceasing when the Zn—KCN ratio has become approximately 1 : 0.6. The results with zinc solutions are not as satisfactory as one would wish, but still they are better than the values obtained by the older methods, which approach more closely the Zn—KCN ratio 1 : 0.

The arguments in favor of the new method are:

(1) Accuracy.

(2) Freedom from interferences.

(3) Rapidity.

(4) Usability in cloudy solutions or solutions containing a precipitate.

(5) Cheapness.

Cornell University,
March 21, 1914.

A lecture delivered by invitation at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914, President E. F. Roeber in the Chair.

ELECTRICAL CONDUCTION AT HIGH TEMPERATURES AND ITS MEASUREMENT.

By Edwin F. Northrup.

I. STATEMENT OF THE PROBLEM.

The older physics recognized only matter and energy as the two objective realities. They were and are still assumed to be conserved in the sense that it is impossible either to bring them into or drive them out of existence. The supply at hand might be made to assume limitless forms and aspects, or it might be squandered by dissipation into space or be so modified in form as to have reduced availability for anything useful. But the total supply of matter and energy in the universe—the capital stock of the scientist and the engineer—is unalterable.

According to the theories of modern physics we must add a third objective reality or entity, the so-called electron, or negative electricity. This theory supposes electricity to be a species of matter or substance, which differs greatly from ordinary matter, but which possesses in common with it the property of being conserved, that is, is uncreatable and indestructible.

These three realities—energy, matter and electricity—are localized in space, and may be transferred from one point in space to another.

Matter is transferred, as when a projectile leaves a gun, from one point in space to another, and this transference of matter may take place whether the space is or is not occupied by other matter. If the matter which is transferred in space is un-electrified, its transference forms no part of the problem of electrical conduction.

Energy likewise may be transferred from one point in space to another, and here again the space may or may not contain matter. The broadcast distribution of electromagnetic energy in

radio-telegraphy is an important form of the transference of energy thru space. The space thru which electromagnetic energy is transferred may or may not have ordinary matter distributed thru it. If the space is filled with matter which is electrically conducting, the electromagnetic energy will move thru space but a short distance, being rapidly converted into heat energy of lower availability. If the space is filled with dielectrics, the electromagnetic energy will advance in the same manner as thru a vacuous space, but with less velocity. The Hertzian resonator is its simplest mode of production. The energy advances by a species of wave propagation. In the advancing wave front there is a magnetic stress at right angles to the direction of energy propagation, and there is an electric stress at right angles to both of these. The energy per unit of volume advances in vacuous space 3×10^5 kilometers per second, and is equally made up of the magnetic and electric stresses.

No matter and no electricity are necessarily associated with the onward movement of electromagnetic energy, which advances with greatest speed and with least hindrance in a perfect vacuum. The problem of electromagnetic energy propagation is, therefore, no part of the problem of electric conduction.

Electricity, to which modern physics assigns a true objective reality, can also move from one point in space to another. Its transference may take place with any velocity short of the velocity of light. If an insulated negatively charged body is carried from one part of a room to another, the eye can follow its transference. We call this slow passage of electricity electric convection. But of two facts we must take cognizance; first, the electric charge did not move through free space isolated and alone, like electromagnetic energy, but on and with a portion of matter, and second, there was present somewhere else an exactly equal charge of positive electricity.

According to modern theory, though we always see negative electricity localized on ordinary matter, it is, nevertheless, itself an objective reality—a sort of substance—and if we divide a charge repeatedly we shall finally arrive at an ultimate unit which can not be further subdivided and to which is given the name electron. This electron is very small, being found,

according to experiments upon the basis of the theory, equal to 4.8×10^{-10} C. G. S. electrostatic units. Modern theory tells us nothing about the size of the positive electric corpuscle, which is somewhere ever present in amount exactly equal to the negative electron. Nor have any experiments ever indicated that the positive electricity may be isolated in space apart and free from a portion of ordinary matter. It is always found associated with and attached to ordinary matter. If a stream of negative electrons (or negatively charged particles of matter) is moving from one point of space to another, as is assumed in gaseous conduction, a stream of positively charged particles of ordinary matter is found moving in the opposite direction. We therefore conclude that *the problem of electrical conduction* consists in examining, and as far as possible explaining, the manner and the laws of the movement of electricity from one point to another point in space which is filled with, or which at least contains, some ordinary matter.

For convenience in treatment, electric conduction is classified into gaseous, electrolytic and metallic conduction, or, more broadly, into gaseous, electrolytic and electronic conduction.

The problem of electric conduction should be further divided into the questions—

(a) Why different materials have a different electrical conductivity at *the same temperature,* and—

(b) Why there is a change in the electrical conductivity of the same substance when there is a *change in the temperature.*

Descriptions of the phenomena of electrical conduction, or theories proposed to explain them, must be considered limited and very incomplete unless these comprehend the phenomena which may be observed over the entire range of temperature which it is possible to produce in the laboratory. It may be maintained that expositions and views presented by expositors of modern physics are inadequate when they fail to see and to describe the phenomena as these are manifested over large temperature ranges. It must be a restricted view which is held by those who elaborate the aspects of physical phenomena in a temperature range which is only one or two percent of the range of temperature producible in the laboratory, and then proceed to develop

theories for the explanation of phenomena which manifest themselves over the entire range of producible temperatures. It is an unwarranted extrapolation. If negative electricity consists of electrons between 20° C. and 100° C., and if its transport consists in a migration of these electrons, then negative electricity must consist of electrons at the temperature of boiling helium or at the temperature of the carbon arc. It is an inadequate theory of electric conduction which must change basic assumptions to meet the observed facts in different temperature intervals. Possibly the modern electron theory will meet these tests but we must first examine the facts, and, incidentally, consider the means which must be employed to increase our knowledge of the facts.

II. THE TEMPERATURE SCALE.

Scientific investigation is a species of exploration and like explorers investigators should begin their inquiries by studying a chart of the field of exploration which lies before them.[1] I have prepared a chart of the temperature scale which I shall explain briefly so we may acquire a better perspective of the problem confronting us.

It is observed that between the absolute zero (—273° C.) and the temperature of the surface of the sun, estimated at 6,000° C. the region of animal life is only about 2.2 percent of the absolute temperature of the sun's surface. It is in this narrow region that the majority of scientific inquiries are confined, and it is in this region that the greatest number of laws and facts regarding nature are known experimentally. As we depart in either direction, from a temperature of about 20° C., nature may be said to grow less and less complex. Thus, slightly above 100° C. all the phenomena of organic life disappear. Above 800° C. magnetic phenomena cease. Above 1,755° C. platinum and a great majority of the metals are molten and metals in the molten state exhibit properties which are independent of the past physical history of the metals. Above 2,000° C. all kinds of matter conduct electricity fairly well. Likewise, at very low temperatures life and chemical activities are less apparent and matter, if not less complex, is at least more quiescent so that many of the com-

[1] A chart was shown at the lecture but is not here reproduced. It was published in Met. & Chem. Eng., June, 1912.

plexities associated with the phenomena of motion have disappeared.

If we call 4,000° C. the highest absolute temperature experimentally realizable, then, since all matter is conducting above 2,000° absolute, the distinction so commonly made between conductors and insulators belongs properly to only the lower half of the producible temperature range.

The advantage of studying electrical conduction at high temperatures results from the fact that we eliminate complexities associated with this problem and hence become able to understand electrical conduction in the temperature ranges where we are accustomed to use it commercially and otherwise.

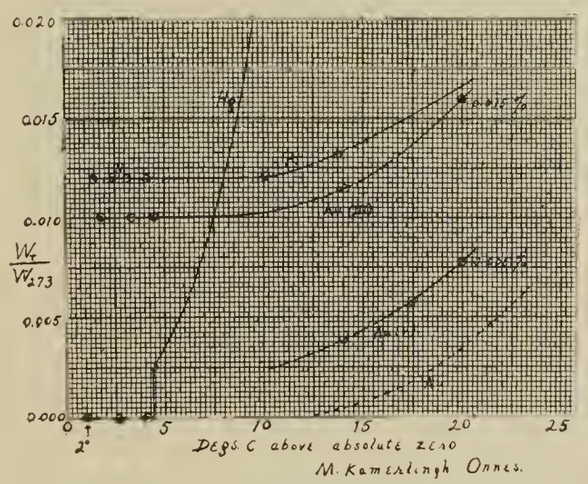


FIG. 1. Curves by Onnes.

III. SOME LEADING FACTS OF CONDUCTION.

While a few investigations of electrical conduction have been extended to within two or three degrees Kelvin and to 1,500° or 1,600° C., our precise knowledge of the facts of electrical conduction is limited, chiefly, to the temperature range 0° to 100° C. Through the work of a few investigators of low temperature phenomena and especially through the researches of M. Kamerlingh Onnes, a few important facts have been obtained regarding the conductivity of matter at very low temperatures. We know, for example, that some at least of the pure metals have a resistivity in the temperature range 2° to about 4.5° Kelvin, which is certainly less than 0.0001 of the resistivity at 0° C. We reproduce here (Fig. 1) some curves obtained by Onnes. He concludes that the curves for platinum and gold would reach, like

the curve for mercury, a conductivity practically infinite, if these metals like mercury could be obtained in a state of purity.

While I am not able to quote authorities it is quite certain that in general the resistivity of the insulators is practically infinite at these extremely low temperatures.

The alloys of the pure metals retain a considerable resistivity even at the lowest temperatures.

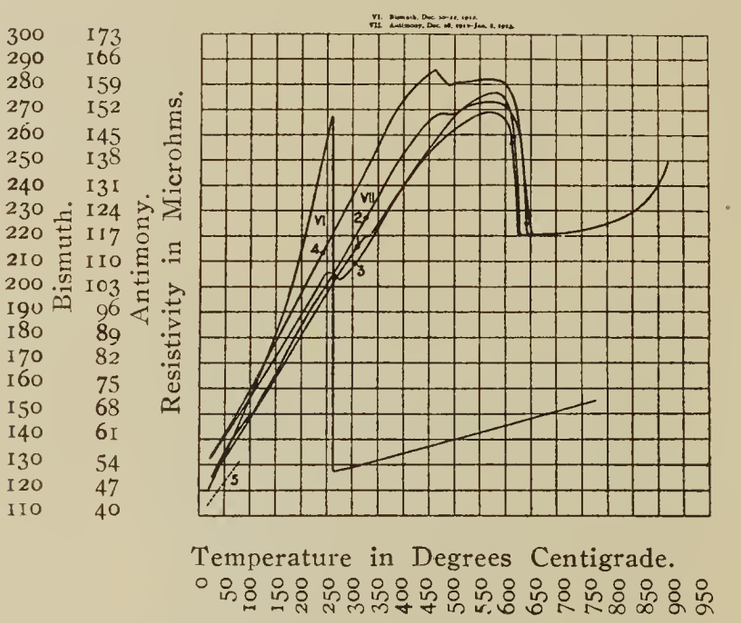


FIG. 2. Resistivity of Bismuth and Antimony.

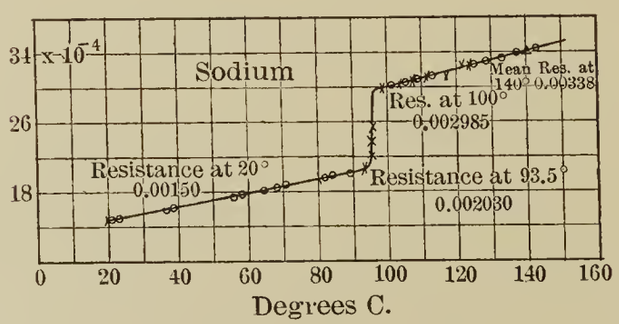


FIG. 3. Resistivity of Sodium.

In studying the electric conduction of metals in the solid state we find, for deducing any general laws, that our problem is much complicated by the fact that the resistivity of the metals is dependent very largely upon their physical state as well as upon their chemical purity and temperature. Thus, whether the metals are in the form of wire, which is hard drawn or soft drawn, or are cast having fine crystals or coarse crystals, depending on the rate of cooling, must influence greatly the values we should

expect to get for their resistivities. The curves reproduced here in Fig. 2 for antimony illustrate the above statement in a striking manner. If comparisons are to be made between the characteristics of the conductivities of the pure metals, we should adopt a means of making these pure metals independent of their past physical history. This means consists, evidently, in reducing the metals to their liquid state, because fusion wipes out the effects

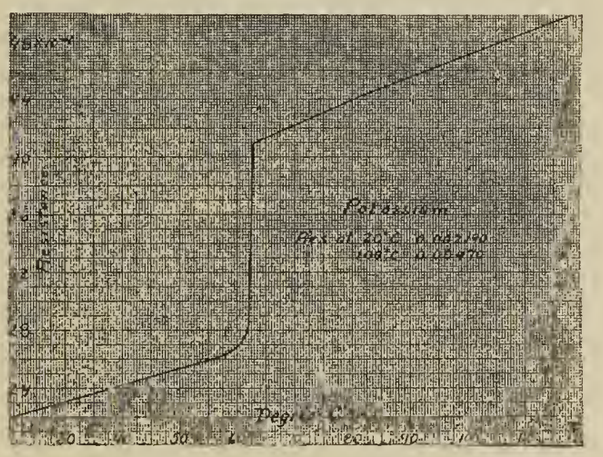


FIG. 4. Resistivity of Potassium.

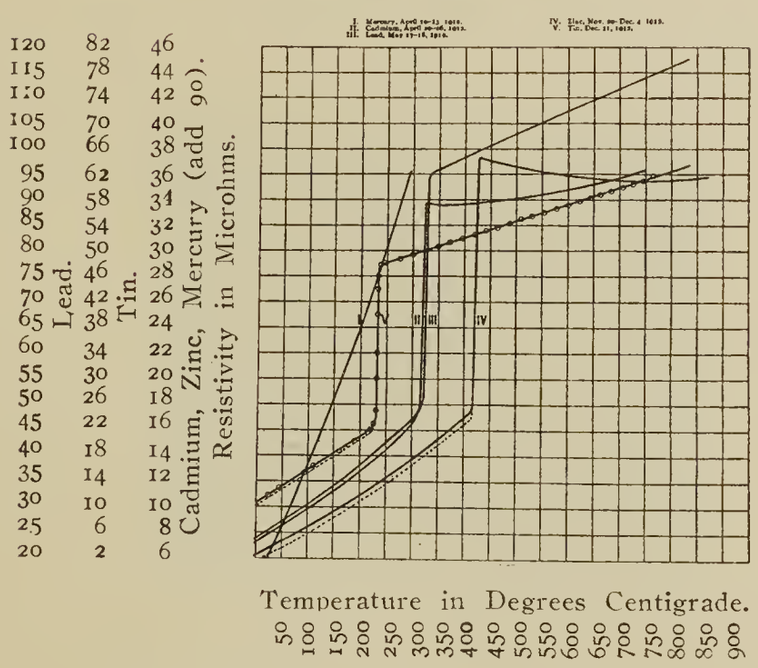


FIG. 5. Resistivity of Hg, Cd, Pb, Zn and Sn.

of all previous physical treatment. The conductivity of metals in the molten state, it is fair to presume, can depend only upon chemical purity, the nature of the metal itself and the temperature, which factors may be controlled. Mercury is the best metal with which to make a fundamental standard of resistance because

it is liquid below 0° C. and can be obtained in a state of very great purity. Its resistivity is independent of its past physical history.

The facts of conduction for the salts, at ordinary temperatures, are very much complicated by the necessity of putting them into

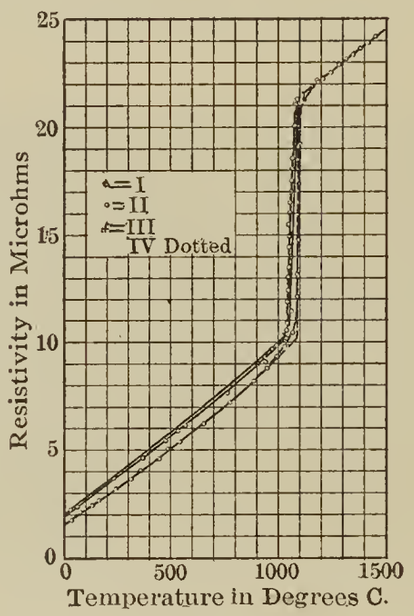


FIG. 6. Resistivity of Copper.

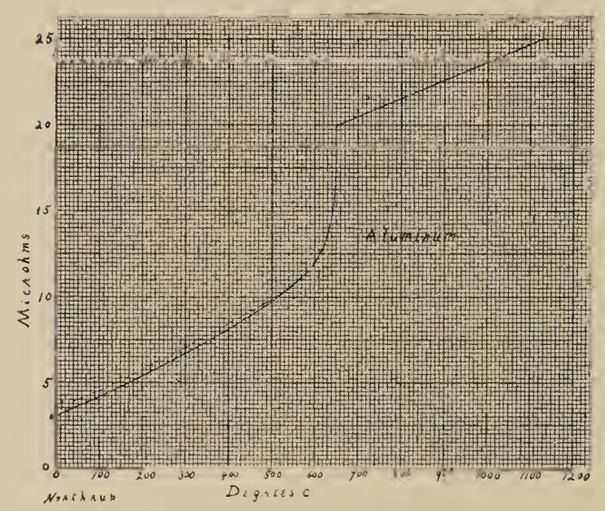


FIG. 7. Resistivity of Aluminium.

solution to make them conducting. They become conducting, however, when molten and their conductivity, like the metals, should, when molten, be independent of their past physical history.

Most metals and salts assume the liquid state only at comparatively elevated temperatures, and, if the obvious advantages

of studying electrical conduction of metals in the molten state have not been utilized heretofore, it is because the experimental difficulties of making accurate measurements at high temperatures had not been overcome. By methods which the author

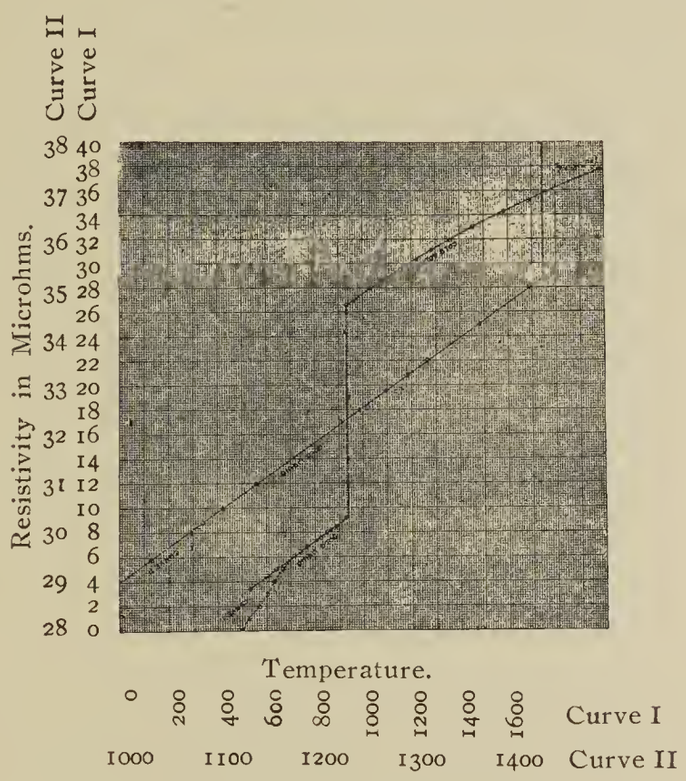


FIG. 8. Resistivity of Gold.

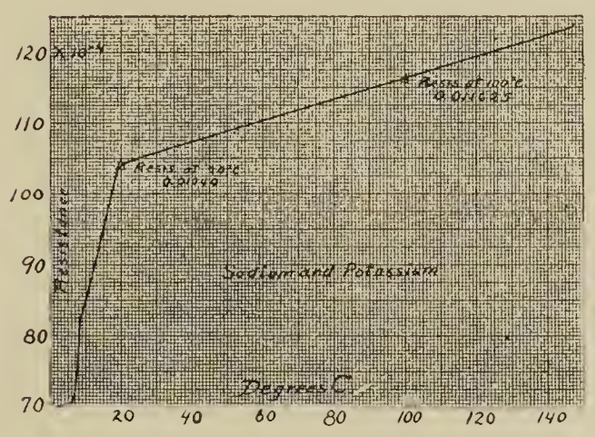


FIG. 9. Resistivity of Sodium-Potassium Alloy.

has elsewhere described[2] many of the experimental difficulties have been removed and metals which melt under 1,500° C., or higher, can have their resistivities determined with errors not much exceeding one-fifth of one percent.

[2] Resistivity of Copper in Temperature Range 20° C. to 1450° C. Jour. Franklin Institute, January, 1914. Also, Resistivity of Pure Gold in Temperature Range 20° to 1500° C. Jour. Franklin Institute, March, 1914.

Methods have also been developed whereby the conductivity of solid compounds may be measured up to 1,600° C. or higher. Somerville has described methods and given curves for the resistivity of metallic oxides to temperatures up to about 1,100° C. His curves (several of which were shown at the lecture) all show a rapid fall in resistivity of these substances with elevation of temperature. The writer has determined the resistivity of alundum up to 1,600° C., as described in Metallurgical and Chemical Engineering, February, 1914. The resistivity of this material (grade RA 355), while practically infinite at room temperature,

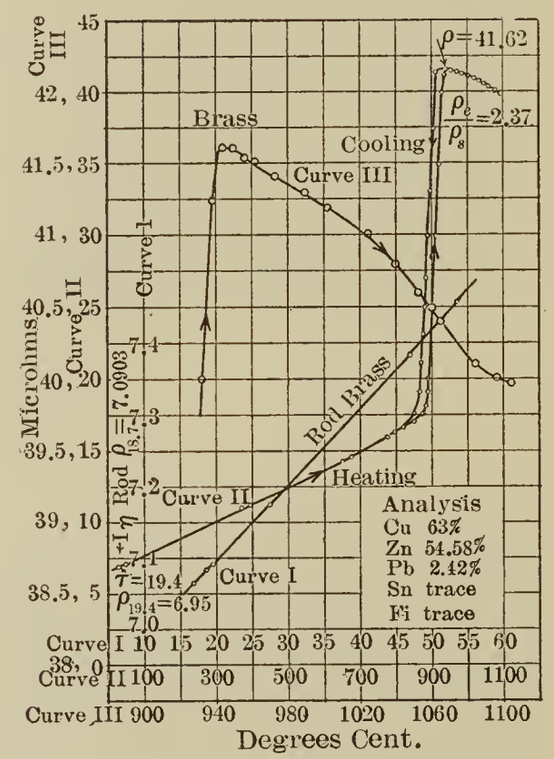


FIG. 10.

falls as low as 190 ohms per centimeter-cube at 1,600° C. The curve has an inflection at 1,100° C. where the resistivity is about 6,100 ohms.

The writer has determined the resistivity of the following metals in the molten state: Na, K, Hg, Cd, Pb, Zn, Sn, Bi, Sb, Cu, Al, Ag, and Au; also the alloys Na + K, equal parts by volume, and brass. The curves of these metals and alloys, with the exception of silver, have all been published in the Journal of the Franklin Institute, the Transactions of this Society, and Metallurgical and Chemical Engineering. We reproduce here

on a greatly reduced scale curves of most of these metals in Figs. 2 to 10.

Attention is drawn to the following characteristics common to the curves for the metals and alloys examined. A change of state is always accompanied by an almost sudden change in resistivity. For metals which expand on liquefaction the resistivity a little more than doubles. For bismuth, which contracts on liquefaction, the resistivity a little more than halves. For antimony, which also contracts on liquefaction the resistivity diminishes. With the exception of zinc and cadmium, metals belonging to the same group, the increase in resistivity with temperature is very nearly linear when the metals are in the molten state. Exception must again be made of antimony, the behavior of which is very erratic in the solid state, and which does not obey a linear law in the molten state.

IV. METHODS EMPLOYED IN MEASURING RESISTIVITIES AT HIGH TEMPERATURES.

The majority of the metals in the molten state oxidize in an oxidizing atmosphere and some absorb hydrogen in a hydrogen atmosphere, and for carrying the temperature to 1,500° C. or higher a furnace of special construction, producing a reducing atmosphere, was developed for the investigation. This furnace has as its heating element pure Acheson graphite. Its heating chamber stands vertical and is cylindrical. This type of furnace has been fully described in Metallurgical and Chemical Engineering, February, 1914. The furnace has been constructed in two sizes and both models were exhibited. The larger model was used in the measurements. Its heating chamber is 12 in. (30 cm.) long and 1⅞ in. (4.8 cm.) in diameter. It will give without strain a temperature of 1,600° C. As it is necessary to determine, in connection with these tests, possible chemical reactions at higher temperatures than those to which the measurements are to be carried an arrangement called *a cascade attachment* was developed. This will slip into the furnace chamber and by its means a temperature of over 3,000° C. may be obtained. Tungsten and molybdenum may be easily melted in this arrangement. As these metals would be in contact, however, with graphite the

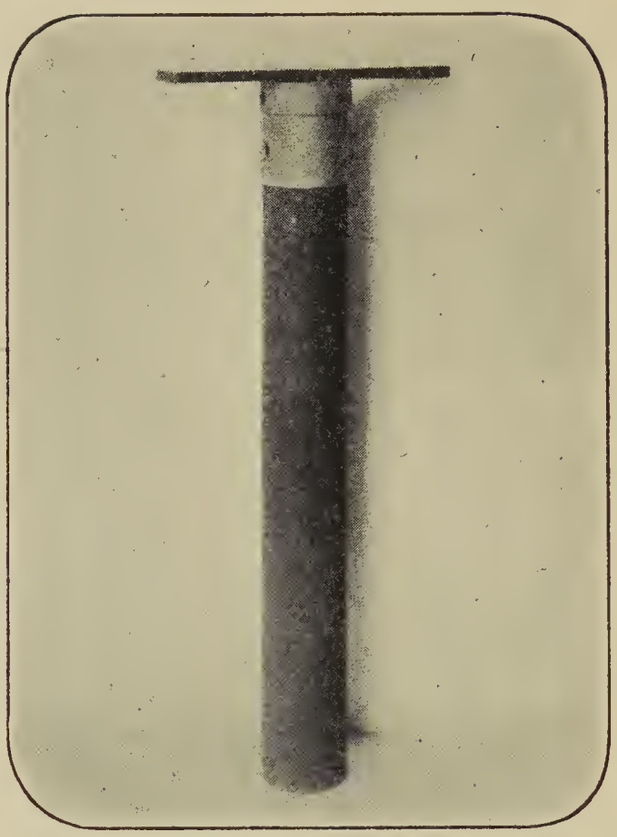


FIG. 11. Cascade Attachment Assembled.

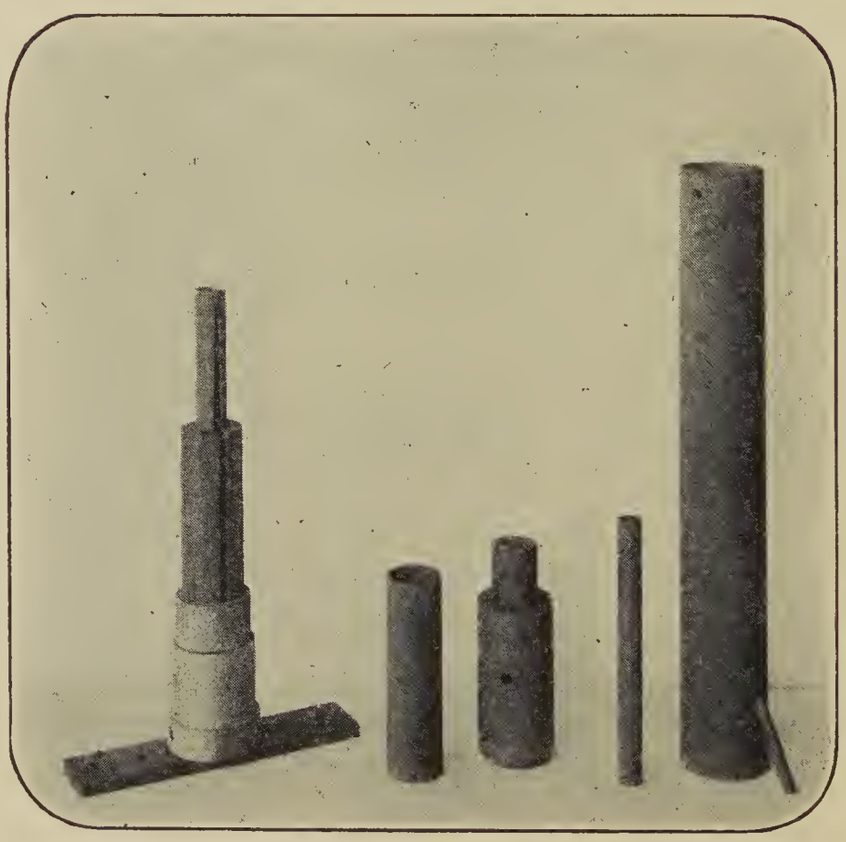


FIG. 12. Cascade Attachment Unassembled.

molten metal would contain carbon and thereby become a carbide. The cascade attachment has been fully described in Metallurgical and Chemical Engineering, May, 1914. It is illustrated in Figs. 11 and 12.

The small model furnace was also exhibited. It will give temperatures above the melting point of platinum and, though not actually used so far for the purpose, would be entirely suitable for measuring the resistivities, especially of the precious metals, by the method as applied using the large furnace. This furnace, not having been previously described, is here illustrated in Figs. 13 and 14.

In all work done by the writer the temperatures were measured with a Pt vs. Pt + 10 percent Rh. thermocouple. At the higher temperatures the thermocouple must be protected in glazed Marquardt ware, or its equivalent.

To hold the molten metals a container of special construction was used. This was shown at the lecture and described. It has already been fully described in the article "The Resistivity of Copper in Temperature Range 20° C. to 1,450° C.", Journal Franklin Institute, January, 1914. All measurements were made with a Kelvin double bridge with ratio coils so chosen that the readings of the bridge multiplied by 10^4 gives the resistivity of the molten metal directly in microhms per centimeter cube. Connections were made with the columns of molten metal (potential and current holes) with connectors of molybdenum wire.

An arrangement was shown called a *double container* which permits the simultaneous measurement of two different metals in the molten state. The two containers are effectually separated from each other by a graphite partition to prevent an intermingling of metallic vapors.

Fig. 15 is a view of the furnace and some of the accessories with which the writer made his measurements.

V. FACTS CONCERNING CONDUCTION AT HIGH TEMPERATURES.

At 1,600° C. or over the insulators have a resistivity of the same order of magnitude, measured in ohms, as the molten metals have, measured in microhms. At these temperatures everything shows considerable conduction. Metallic vapors conduct and

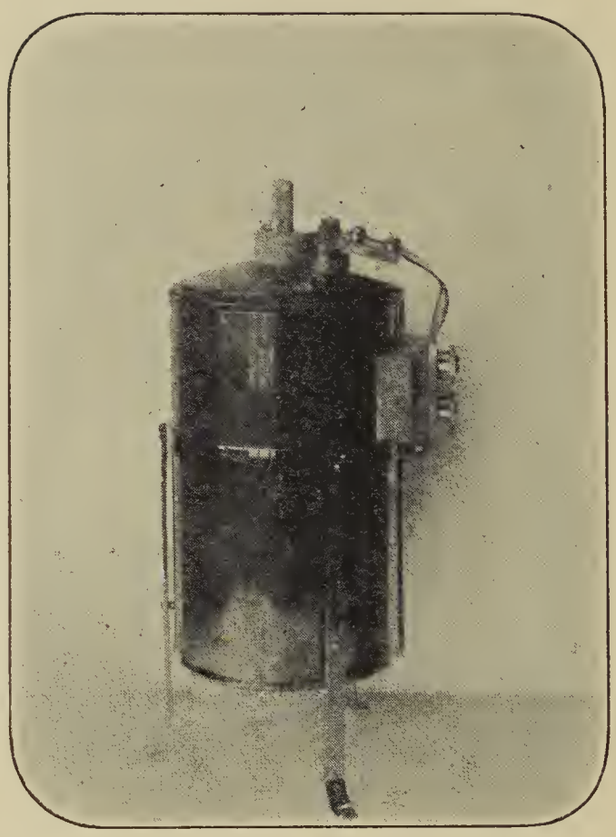


FIG. 13. Small Furnace Assembled.

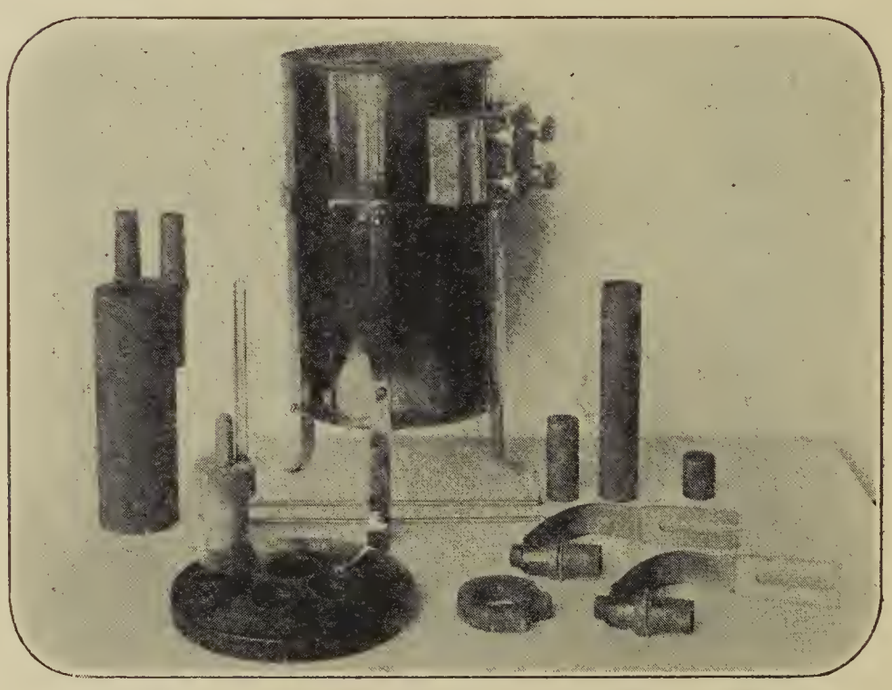


FIG. 14. Small Furnace Unassembled.

considerable current can be passed, under a pressure of 110 volts A. C., through the atmosphere generated in the furnace chamber. Most pure metals have curves so nearly linear in the molten state that the increase with temperature of the resistivity of a molten metal may be used to measure with precision a high temperature in a laboratory furnace.

A summary of the more interesting features of the pure metals examined by the writer are given in Table I, which is self-explanatory. The tenth column of this table brings out the

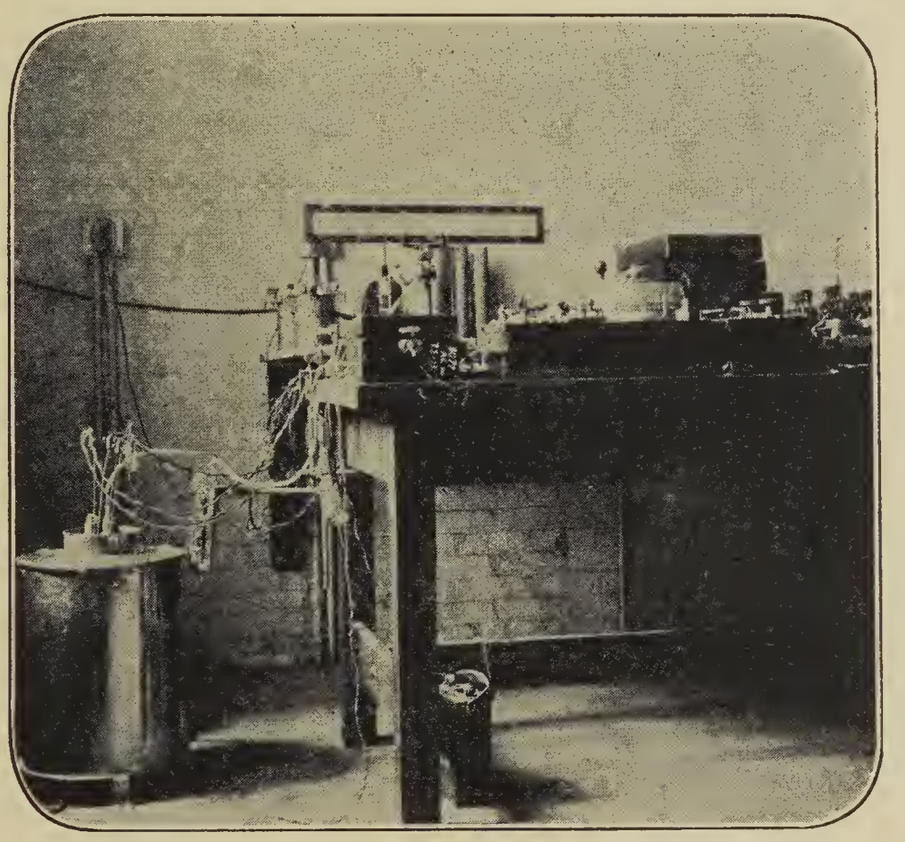


FIG. 15. Furnace and Accessories.

interesting fact that the ratio of the co-efficient of resistance to the co-efficient of cubical expansion of at least six of the metals, when the two co-efficients are figured from the same temperature, is closely the same for the different metals.

The hypothesis is forcibly suggested by the facts that with increasing temperature the increase in resistivity of the pure metals is closely associated with the increase in separation of the atoms or molecules of the metals. The writer believes, however, that the time is not yet ripe for propounding a theory of metallic conduction which will cover the facts brought out by investiga-

TABLE I.

1	2	3	4	5	6	7	8	9	10
Element	Melting Point Degrees C	ρ_s = Resistivity just before Fusion	ρ_l = Resistivity just after Fusion	$\frac{\rho_l}{\rho_s}$	Gram Calories to Melt One Gram	Volume After Fusion / Volume Before Fusion	Coef. of Cubical Expansion at Temp. t	Coef. of Resistance at Temp. t	Coef. of Resistivity / Coef. of Cubical Expansion
Sodium . . . . . I. Na 23	97.	6.75	9.656	1.43	31.7	. . .	834×10^{-6} $t = 100$	3300×10^{-6} $t = 100$	3.96
Aluminum . . . . III. Al 27.1	657.	12.5 ?	20.13	1.6	77.	. . . .	. . . . .	509×10^{-6} $t = 657$	. . . .
Potassium . . . . . I. K 39.1	62.5	8.74	13.35	1.53	15.7	. . . .	900×10^{-6} $t = 70$	3602×10^{-6} $t = 70$	4.00
Copper . . . . . I. Cu 63.57	1083.	10.20	21.30	2.088	43.	1.03 ?	. . . . .	372×10^{-6} $t = 1100$	. . . .
Zinc . . . . . II. Zn 65.37	418.	17.0	37.3	2.19	28.	. . . .	. . . . .	Not Linear	. . . .
Cadmium . . . . . II. Cd 112.4	321.	17.1	33.77	1.97	13.7	. . . .	. . . . .	Not Linear	. . . .
Tin . . . . . IV. Sn 119	232.	22.0	47.4	2.15	14.2	1.027	89.8×10^{-6} $t = 500$	479×10^{-6}	5.34
Antimony . . . . . V. Sb 120.2	630.	152. Variable	117.	0.7 to 0.8	. . . .	. . . .	. . . . .	Not Linear	. . . .
Gold . . . . . I. Au 197.2	1063.	13.5	30.82	2.283	. . . .	. . . .	. . . . .	451×10^{-6} $t = 1100$	. . . .
Mercury . . . . . II. Hg 200	— 38.8	36.5	80.6	2.20	2.72	. . .	181×10^{-6} $t = 100$	938.7×10^{-6} $t = 100$	5.19
Lead . . . . . I. Pb 207.1	327.	38.7 ?	95.0	1.95 ?	5 37	1.029	113.1×10^{-6} $t = 500$	435×10^{-6} $t = 500$	3.85
Bismuth . . . . . V. Bi 208	269.	267.	127.5	0.478	12.6	$< 1.$	120×10^{-6} $t = 271$	417.8×10^{-6} $t = 271$	3.48

tions over very wide temperature ranges. More observations must be made and related physical properties of the metals must be more carefully studied over the same temperature ranges for which the resistivities are determined.

VI. INVESTIGATIONS FOR THE FUTURE.

The problem of electric conduction, it seems to the writer, is most likely to be solved by studying the resistivity of metallic vapors under pressure. If possible the resistivities of several liquid metals should be measured as they pass from the liquid to the vaporous condition under temperatures and pressures which are near the critical values.

Precise knowledge is needed of the cubical expansion coefficients of the molten metals. Also the changes in volumes which occur when the metals pass from the solid to the liquid state.

All the metals, in all cases where it is physically possible, should have their resistivity curves determined from their melting point to their vaporization point. Then any theory of metallic conduction which is fully adequate must account for all the facts which such an extended investigation would reveal.

We know much less concerning the underlying causes which determine the resistivity at a given temperature and the variation in the resistivity with temperature of an alloy than we do of a pure metal. It is important, therefore, to study the resistivities of a large number of carefully chosen alloys in the molten state. As most alloys have lower melting points than pure metals the methods applied to the pure metals may be with even greater ease applied to these. Incidentally the writer is convinced that the tracing of the resistivity curve from the molten into the solid state is easier to apply and will give more information than is given in the ordinary way by obtaining the cooling curve. For example, note the information which the resistivity curve gives respecting brass. The curve plainly shows that at about 1,090° C. the brass has begun to lose zinc by vaporization of this metal.

The study of the electrolytic conduction of fused salts, the writer believes, would result in yielding valuable information regarding the nature of conduction.

The electric conduction of compounds at high temperatures could not be studied with advantage as far as giving scientific information regarding the problem of electric conduction is concerned, but the facts obtained would be commercially useful for designers of electrothermic apparatus.

The writer feels that he has but made a beginning in the investigation of conduction at high temperatures but he hopes to continue his researches in this direction and that he may be aided by others becoming interested in the same problem.

Palmer Physical Laboratory,
Princeton, N. J.

DISCUSSION.

C. G. FINK: Were the molybdenum electrodes dissolved to any extent in the molten copper at 1500° C.

E. F. NORTHRUP: At 1500° C. copper wets molybdenum in the same way that mercury wets copper, but will not penetrate it. Molybdenum does not dissolve in and thus contaminate the copper at 1500° C.

C. G. FINK: What was the atmosphere?

E. F. NORTHRUP: We worked only with a CO atmosphere, though some nitrogen from the air was probably present.

JOSEPH W. RICHARDS: If I understood Dr. Northrup aright, the ratio of resistivity in the liquid state to that in the solid state, at the melting point, is nearly the same for the different metals; in the next column he has the latent heat of fusion, and states that there is no connection between it and the ratio of resistivities at the melting point.

E. F. NORTHRUP: None that I can discover.

JOSEPH W. RICHARDS: I think I can show the connection between them. If I remember aright, the ratio for copper is 2.09. The melting point of copper is 1084° C., adding 273 you have 1357° absolute. The product of 1357 by 2.09 is 2836; divide that by the atomic weight of copper, and you get 44.6. You have

the latent heat of fusion, 43. Multiply it (the atomic weight) by the latent heat of fusion (absolute temperature of the melting point), and you get the atomic latent heat 2735, instead of 2836. This is near enough to 2836 to make the matter interesting.

E. F. NORTHRUP: Have you the data on bismuth, which decreases in resistivity after liquefying?

JOSEPH W. RICHARDS: I have not the figures in my mind at the moment, but I think you will find that bismuth will agree. I picked out copper because I happened to have the figures in mind, and it agrees, and I think you will find it agrees with the others, excepting perhaps in the case of the anomalous metals, bismuth and antimony.

E. F. NORTHRUP: I have had a feeling that the input of energy to convert the metal from the solid into the molten state must in some way have a relation with the change in resistivity, but I have not as yet been able to trace any relation myself, and if Dr. Richards can throw light on this subject I shall certainly welcome it very much.

P. M. LINCOLN: Referring to the curves that were shown for molten metal, were they taken for a constant volume or a constant weight; in other words, was the expansion of the material while molten taken into account? While the metal is solid we have a constant weight under observation. The question I ask is whether, when the metal is molten, we have a constant weight under observation, or a constant volume?

Another question is in regard to the projection of the curves. A number of the metals show that the curve was perfectly linear after the metal had reached the molten state. If the curve were projected toward zero temperature, and the metal remained molten clear down to zero, would the curve pass through the origin?

E. F. NORTHRUP: The first question is answered by stating that all my determinations of the resistivities of the metals in the molten state were made with a constant volume, and not with a constant mass. There is a good deal of confusion in making measurements of this character as to just what one is doing, but I was very careful to be clear on this matter. Of course, at

the extent to which the material of the container expands or shrinks, the measurements are not at constant volume, but the expansion or shrinkage of the container I consider to be extremely small. I have tried projecting these curves down, and find that they do not anywhere near cross the temperature axis at the absolute zero.

P. M. LINCOLN: Which way?

E. F. NORTHRUP: They extend far below the absolute zero.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

LABORATORY NOTES ON SOME ELECTRICAL PROPERTIES OF SILVER SULPHIDE

By F. A. J. FitzGerald.

Some time ago it was necessary to study some of the electrical properties of silver sulphide in relation to the commercial development of an automatic fire alarm invented by Mr. Eugene Garretson, and a selection from the laboratory notes made during the prosecution of the work seems worthy of publication.

The principle of the fire alarm consists in the use of a substance having a negative temperature coefficient of electrical resistance. A thermoscope is made by mounting the substance in a suitable holder so that it may be inserted in an electric circuit, which also includes an indicating device in the shape of a telephone drop and an alarm gong. Under ordinary temperature conditions the resistance of the thermoscope is so high that the current is not sufficient to work the drop, which in turn would close the gong circuit. If, however, the temperature of the surroundings of the thermoscope rises, its electrical resistance decreases, thus increasing the current, which tends to raise the temperature of the thermoscope till finally a point is reached where the current is sufficient to work the drop and give the alarm.[1]

The thermoscope as originally made by Garretson had as the active element a strip of silver sulphide about 10 mm. (0.39 inch) long, 5 mm. (0.20 inch) wide and 0.5 mm. (0.02 inch) thick. To the ends of this strip pieces of copper wire were fused for making connection with the terminals of the holder. The thermoscope was used in a circuit containing three dry batteries.

When the laboratory study was begun it was soon found that Garretson's thermoscope was by no means a permanent apparatus,

[1] "A New Automatic Fire Alarm," by F. A. J. FitzGerald, Journal of the Franklin Institute; November, 1913.

for, although it had, when first put into the circuit, a resistance of 1 or 2 megohms, this gradually decreased until after some days or weeks the resistance would only be a few ohms, allowing sufficient current to work the drop and give the alarm. Thus it became necessary to work out a practical application of Garretson's invention, and this was eventually done, with the result that thermoscopes can now be made not only for use as fire alarms, but to give warning of overheating of bearings, transformers, cable conduits, etc.

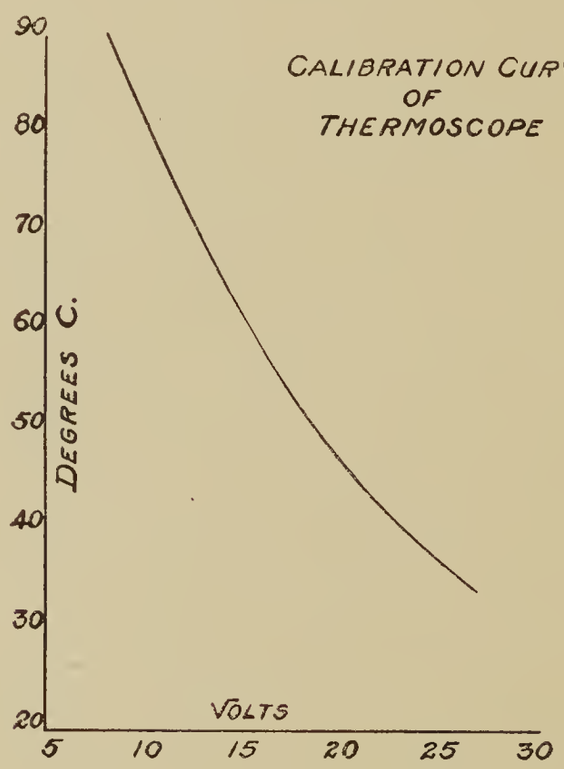


FIG. 1.

In Fig. 1 is shown a typical calibration curve of a thermoscope, giving the temperatures at which alarms are rung with various voltages in the circuit. It was incidental to the work of developing the thermoscope that the following notes were made.

ELECTROLYTIC EXPERIMENTS.

I.

It was evident that the failure of the thermoscopes on a direct current circuit was due to electrolysis of the silver sulphide with the formation of a thread of metallic silver which connected the anode and the cathode. It was afterwards found that this

phenomenon had been observed by Lorenz[2] several years ago. Some experiments on the electrolysis of silver sulphide were made.

A piece of silver sulphide of the form used in the thermoscopes was made by heating a plate of pure silver in molten sulphur, and mounted in the usual way. The resistance was determined as 1.87 megohms at 18° C. At 58° C. the resistance was 0.334 megohm.

The thermoscope when put in a direct current circuit with an e. m. f. of 24 volts worked an 80-ohm telephone drop at 58° C. The resistance was then measured at this temperature and found to be 0.0580 megohm. Cooled to 22° C. the resistance was only 0.274 megohm.

II.

Another thermoscope was found to have a working temperature of 160° C. in a 10-volt D.C. circuit. It was then allowed to cool and again put in the 10-volt D.C. circuit, where after a time it became a sufficiently good conductor to work the telephone drop. It was then put in a 10-volt, 25-cycle A.C. circuit and found to carry a working current, but after a few seconds the resistance increased and was apparently as high as when the thermoscope was first made.

The thermoscope was then put in the 10-volt D.C. circuit, and after a time again carried the working current. The battery connections were reversed and the thermoscope no longer carried a working current; but after a lapse of 5 hours its resistance had again dropped to the working point. Finally it was returned to the 10-volt A.C. circuit, where after carrying a working current for a few seconds it recovered its high resistance, and it was only after the lapse of a week in the A.C. circuit that it finally broke down.

The explanation of the phenomena is apparently as follows: When put in a D.C. circuit, metallic silver is formed on the cathode, and thus gradually builds up a conducting path between the electrodes. If the polarity is reversed the heating effect of the current is sufficient to convert the thread of metallic silver to silver sulphide, and the resistance is again high until

[2] Elektrolyse geschmolzener Salze, Vol. II, p. 169.

there is a conducting path formed between the new cathode and anode. On the other hand, when the thermoscope is put in the A.C. circuit the heat developed is sufficient to re-form the sulphide, and, as there is presumably no electrolysis, the thermoscope preserves its high resistance.

This does not explain the ultimate failure in the A.C. circuit; but that will appear later.

III.

An experiment to confirm the conclusions arrived at in II was made as follows: A strip of silver sulphide was coated with a thin layer of sulphur and put in a 4-volt D.C. circuit until it carried current *without appreciable heating,* showing that a good metallic connection was formed between the anode and cathode. It was then put in a 5-volt A.C. circuit and carried a working current readily. It was next put in a 10-volt D.C. circuit, but with the former cathode as anode, and presently became so hot as to set fire to the sulphur with which it was coated, when it was immediately removed and allowed to cool. Put now in a 10-volt A.C. circuit, it no longer carried an appreciable current.

IV.

A quantity of pure silver sulphide was melted with an excess of sulphur and then allowed to cool down in a covered crucible. From the ingot obtained in this way a disc 20 mm. (0.79 inch) long and 2.5 mm. (0.10 inch) thick was ground. After polishing the faces of the disc it was clamped between two polished discs of artificial graphite, which thus formed the electrodes of the silver sulphide cell. This was put in a D.C. circuit with a voltmeter and ammeter, and the following readings taken:

Time	Volts	Amperes
0 min. 00 sec.	9.6	0.110
0 30	9.8	0.030
2 00	9.9	0.019
5 00	10.0	0.010

When removed from the circuit and connected directly to the voltmeter the cell gave a reading of 0.1 volt.

After leaving the cell in the D.C. circuit again for 5 minutes it was connected to a Leeds and Northrup moving-coil galvan-

ometer, resistance 107 ohms. The reading was off the scale, but rapidly diminished to 110 mm., and then very slowly decreased until it reached zero.

The cell was then put in the 10-volt, 25-cycle A.C. circuit for a few minutes, and when again connected to the galvanometer gave a deflection of 60 mm. The polarity of the cell in this case was the same as when taken from the D.C. circuit.

The cell was put in the 10-volt D.C. circuit, but with the former cathode as anode, and when then connected to the galvanometer the deflection was reversed. This was repeated several times, and invariably the electrode connected to the positive pole of the D.C. circuit was positive when tested with the galvanometer.

V.

After experiment IV the cell was taken apart, but in doing so the electrodes and silver sulphide disc were marked so that they could be put together in the same relative positions as before. It was observed that the electrodes tended to stick to the silver sulphide, and, when examined under a microscope, both showed a deposit having a metallic appearance. The electrodes were then well cleaned and polished, and the cell put together in the same way as before. It was now put in the 10-volt A.C. circuit for a few minutes, and then connected to the galvanometer. A deflection of 50 mm. was observed, the direction being the same as the last time the cell had been taken from the 10-volt D.C. circuit. Finally the cell was again taken apart, the faces of the electrodes ground down and polished, and the cell put together as before. When connected in the galvanometer circuit it gave a small deflection in the same direction as the last.

VI.

A cell similar to that used in experiments IV and V was made, but the silver sulphide disc was only 0.28 mm. (0.11 inch) thick. With an e. m. f. of 0.5 volt this cell carried 1.3 amperes. Connected to the galvanometer it gave a deflection off the scale, but this diminished rapidly. Determinations of the rate of discharge under different conditions were made:

(1) Connected permanently in galvanometer circuit.
(2) On open circuit.
(3) Short circuited.

The method followed was to note the time elapsed between a deflection of 160 mm. to about 60 mm. with a stop-watch. In the case of the open circuit and short circuit determinations a switch was used so as to connect at intervals with the galvanometer.

1. Time of discharge from 160 to 60 mm. with cell in galvanometer circuit.....163 secs.; 0.61 mm. per sec.
2. Time of discharge from 160 to 58 mm. with cell on open circuit.....173 secs.; 0.59 mm. per sec.
3. Time of discharge from 160 to 53 mm. with cell short circuited.....176 secs.; 0.61 mm. per sec.

There is therefore no appreciable difference in the rate of discharge. This may, however, be explained by an internal short-circuit in the cell, since, as was shown by experiment IV, a cell with a thick electrolyte may discharge very slowly.

RESISTANCE DETERMINATIONS.

In making determinations of the electrical resistance of silver sulphide the ordinary bridge method was used with current supplied by a small induction coil and a telephone receiver in place of a galvanometer. The determination of the resistance of the standard thermoscope is unsatisfactory if it is exposed to the air of the room because of its extraordinary sensitiveness to changes of temperature. Precautions must also be taken to avoid the introduction of a serious error due to the heating effect of the testing current, as is well shown by the following experiment.

VII.

A small cell similar to that used in Experiment IV, but with silver electrodes, was made. Its resistance was determined, with the following results:

Ratio	Coils	Bridge Coils	Cell
1000	1000	1650	1650
100	1000	176	1760
10	10	2800	2800

In the three determinations made above, the ratios between the resistances of the circuits into which the testing current divides are respectively 1:1.65, 1:1.75 and 1:2.80, hence the current density in the strip of silver sulphide is much higher in the first than in the last determination.

It is therefore necessary to use as small a testing current as practicable, to immerse the piece of silver sulphide under test in an oil bath provided with a sensitive thermometer, and to keep the oil circulating freely. These conditions were maintained in the following experiments.

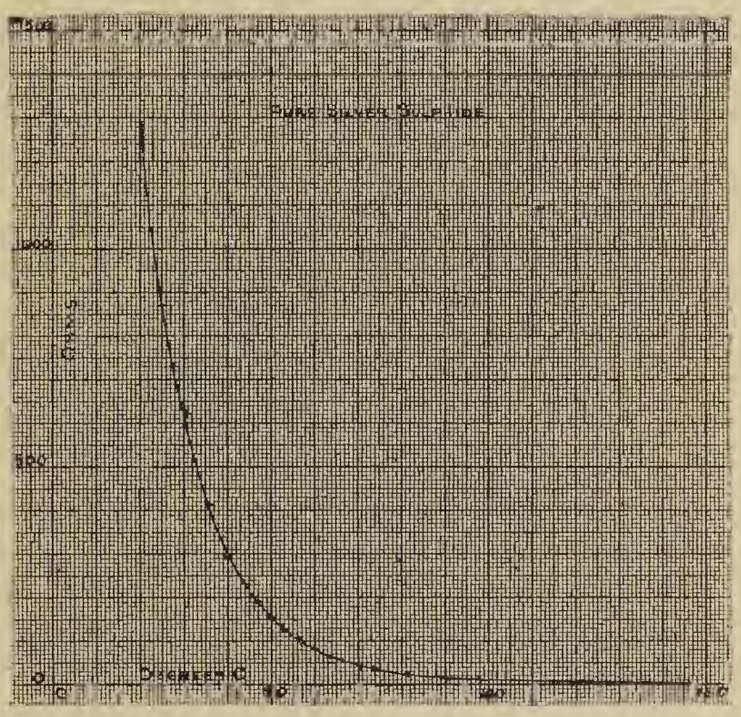


Fig. 2.

VIII.

A cell similar to that of Experiment VII was used for resistance determinations at various temperatures, and the results obtained are shown in the curve of Fig. 2. This may be taken as typical of silver sulphide as far as it goes; but if the temperature is carried to a higher degree the character of the curve is changed.

IX.

It was thought that the cell used in Experiment VIII was not a satisfactory form, as the heating effect of the testing current might be appreciable, or at least it was likely that the silver sulphide and the oil bath would not be at the same temperature. Accordingly a small ingot of silver sulphide was cast, and from this a rod turned in the lathe 45 mm. (1.77 inches) long and 5.7 mm. (0.22 inch) in diameter. The rod was threaded for a distance of 10 mm. (0.4 inch) at each end, and screwed into silver

terminals 15 mm. (0.6 inch) long and 10 mm. (0.4 inch) in diameter.

Resistance determinations of the rod were made at various temperatures, and the results are shown in the temperature-resistance curve of Fig. 3 from 120° up, since at lower temperatures the general character of the curve is similar to that of Fig. 2. A sudden change of resistance is observed at 162°. The percentage proportions of silver and copper in the sulphide used for this experiment are given because the copper has an important influence on the critical temperature.

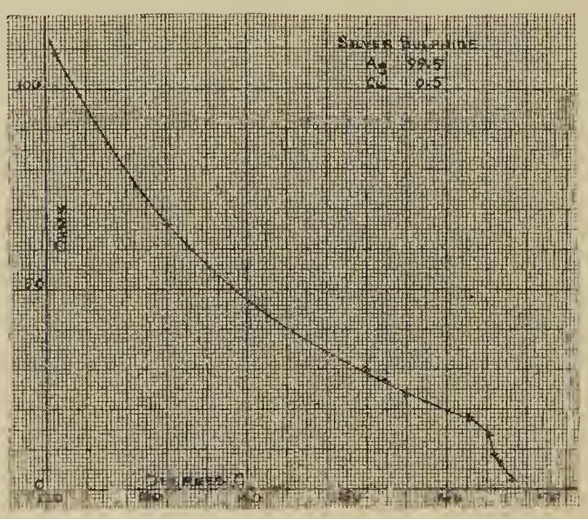


Fig. 3.

X.

A rod similar to that used in Experiment IX was made of sulphide prepared from an alloy of sterling silver (92.5 percent Ag and 7.5 percent Cu), and its temperature-resistance curve determined. The results are shown from 100° up in Fig. 4. Here we again have a critical temperature, but instead of this being 162° it is about 104°.

XI.

Two thermoscopes were made up in the usual manner, and their temperature-resistance curves determined, with the results given in Fig. 5. This shows very clearly the different critical temperatures of a sulphide prepared from pure silver and one from the sterling silver alloy: 170° and 104° respectively. It may also be noted that the critical temperature for the sulphide made from

pure silver is somewhat higher than that observed in the case of the alloy containing 0.5 percent copper.

Before leaving the resistance experiments there are a few observations in relation to them which should be recorded. All the resistance-temperature curves shown are from determinations made with *rising* temperature. It has been observed that the measurements of resistance made with falling temperature may not correspond with those obtained when the temperature was rising. If in a series of determinations the maximum temperature

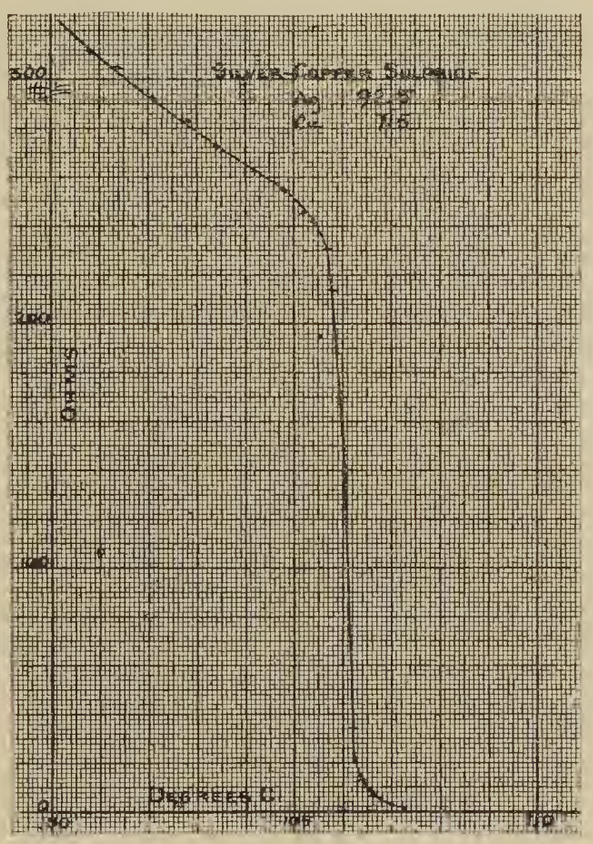


FIG. 4.

reached is well below the critical temperature, then the determinations of resistance, heating and cooling, lie approximately on the same curve. On the other hand, if the temperature is carried beyond the critical point the cooling curve is not the same as the heating curve, and it is necessary to cool to a temperature several degrees below the critical point found with rising temperatures before another critical point is found, where a sudden increase in resistance occurs. Below the critical temperature found on the cooling curve, resistances may again follow the same curve. No curves illustrating this observation are given, for the experiments made were too few.

Another observation should be kept in mind. In the process of making the thermoscopes, or in making castings of silver sulphide, oxidation with the formation of metallic silver may occur, and even the presence of a minute amount of metallic silver may seriously affect the resistance of the sulphide. This at least appeared to be the explanation of an anomaly found in the case of a rod of the silver sulphide used in Experiment IX. When the resistance of this rod was measured at 20° it was found to be only 1400 ohms, which was low judging by former

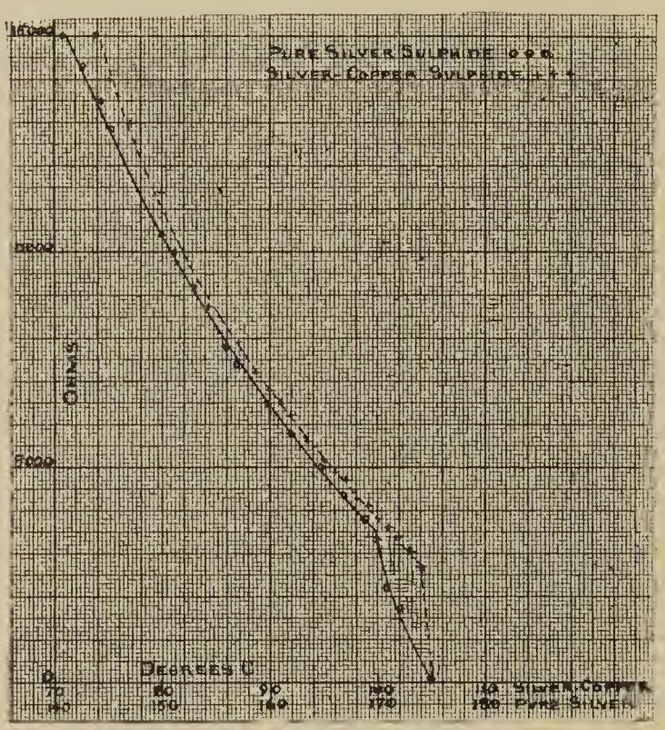


Fig. 5.

experience, so an analysis was made to determine the silver and copper present and the results obtained calculated to silver and copper sulphide=

Silver sulphide	99.56
Copper sulphide	0.55
	100.11

While the total for this analysis is not unsatisfactory, the small error indicated the possibility of the presence of free metal. Accordingly the rod was boiled for a few hours in a saturated solution of potassium sulphide, thoroughly washed with water, and the threaded ends put through the die-plate again. On then measuring the resistance it was found to be 70,000 ohms.

When sterling silver is used for the manufacture of the sulphide another disturbing factor is introduced, due to the difficulty of obtaining a homogeneous alloy. The attempts made to produce alloys of silver and copper in our laboratory were unsuccessful, for when the ingots were rolled into sheets and plates the sulphide made from them was useless for the manufacture of thermoscopes, different pieces varying enormously in resistance. This was found to be due to segregation in the alloy. The sterling silver alloy now used is specially made for us by Baker & Co., and is excellent for commercial purposes. Nevertheless, microscopical and metallographical examination indicate that even the sulphide from this alloy is not perfectly homogeneous, and this certainly influences the resistivity and other electrical properties which will be presently considered.

THERMOELECTRIC EXPERIMENTS.

As thermoelectric effects might be expected with the silver sulphide, a few experiments were made on this point, since these would influence other observations.

XII.

A thermoscope was connected to the galvanometer, and one of the junctions between the sterling silver sulphide and the copper touched with a hot wire. The galvanometer coil was instantly deflected, but quickly returned to zero. When the other junction was touched the deflection was in the reverse direction.

XIII.

The galvanometer was connected to one pair of terminals of a double-pole double-throw switch, the other pair connected to a 10-volt, 25-cycle A.C. circuit, and a standard thermoscope socket to the terminals of the switch blade. With this arrangement any thermoscope could be tested by putting it in the socket, connecting it to the transformer circuit by closing the switch for a minute, and then throwing the switch over so as to read the galvanometer deflection, if there were any. A large number of thermoscopes were examined in this way, and the following observations made with different thermoscopes:

(1) No deflection.
(2) Fairly constant deflection.
(3) Deflection quickly diminishing to zero.
(4) Deflection quickly diminishing to fairly constant deflection in same direction.
(5) Deflection quickly diminishing to fairly constant deflection in opposite direction.

The thermoelectric e. m. f. is evidently caused by unequal resistance of the junctions of the copper wire and sterling silver sulphide, and this is sometimes superimposed on an electrolytic e. m. f.

ELECTROLYSIS IN A.C. CIRCUIT.

It will be recalled that in Experiment II it was found that a thermoscope broke down in an A.C. circuit after the lapse of a week. This led to experiments to find out the cause of this failure. A number of experiments which need not be detailed showed that it was not due to external causes, such as some chemical action from the laboratory fumes or anything of that nature, but must be looked for in the thermoscope circuit. Statistical experiments on a large number of thermoscopes gave some interesting results. For example, it was observed that the time which elapsed before thermoscopes failed was very variable; given any number of thermoscopes under observation, the rate at which the defective ones revealed themselves depended on the voltage; defective junctions between the wires and the silver sulphide were correlated with failures.

It was also recalled that some years ago Garretson had patented an "Electric Valve," which is made by using a disc of oxidized brass in contact with a disc of silver superficially coated with silver sulphide.

Finally the hypothesis was reached that the failures were due to electrolysis caused by a rectifying effect of the thermoscopes and experiments undertaken to test its usefulness.

XIV.

A plate of pure silver sulphide was clamped between two plates of copper, one of which had a well polished surface, while the other had a thin coating of cupric oxide. A similar cell was made with both copper plates well polished. A circuit was then made which would include either of these cells, 4 dry batteries con-

nected in series, a 6-volt incandescent lamp, a milliammeter and a reversing switch so that the direction of the current through the cell could be changed. When the cell with the two polished copper plates was put in the circuit it was found that the current was the same no matter which way the cell was connected in circuit. But if the cell with the electrode coated with cupric oxide was used, and the clean copper electrode was +, a current of 0.6 ampere was obtained, while on reversing the current so as to make the coated electrode + there was a momentary current sometimes great enough to make the lamp flash up, but immediately dropping to 0.01 ampere.

This demonstrated the possibility of a rectifying effect in thermoscopes with copper wire connections, and the next problem was to detect the rectifying effect, if there were any, in the thermoscopes. This was done in the following manner.

XV.

Referring to Fig. 6, G is the Leeds & Northrup galvanometer, R a resistance of 10,000 to 100,000 ohms, variable in steps of 10,000 ohms, C is a 25-cycle transformer with a primary e. m. f. of 110 volts and a secondary giving 5 to 30 volts in 5-volt steps, T is a thermoscope which is immersed in the oil bath O provided with thermometer, stirrer and heating coil, S is a double-pole, double-throw switch so wired that when closed on the right-hand side the transformer secondary, thermoscope, galvanometer and resistance are in series. On the other hand, when the switch is closed on the left-hand side, the thermoscope, resistance and galvanometer only are in series, and the transformer is cut out of the circuit. *It is important to observe that in changing the switch the relative connections of the galvanometer and thermoscope are reversed.*

It was found, as might be expected, that when a conductor of the first class, such as an incandescent lamp, was substituted for the thermoscope, and the transformer circuit was closed, there was no deflection of the galvanometer. When, however, a thermoscope was put in the circuit there was in general a deflection of the galvanometer. This, of course, does not mean the momentary kick which almost invariably occurs, but a more or less steady deflection. Thus out of a set of standard thermo-

scopes made of the sterling silver sulphide only 3 gave no appreciable deflection, the rest all giving deflections varying from 1 to 180 mm. on the scale with a transformer e. m. f. of 20 volts and R = 10,000 ohms.

This indicates that most standard thermoscopes have a rectifying effect which would explain the failure on A.C. circuits.

XVI.

A statistical experiment was made on 41 standard thermoscopes by determining the galvanometer deflection for each and then putting them in a 20-volt A.C. circuit. After the lapse of 3 days 17 thermoscopes had broken down; but subsequently there were no failures. In general all thermoscopes giving deflections of 30 to 180 mm. broke down within 15 hours, while those showing smaller deflections lasted somewhat longer. Those showing very small deflections (1 to 5 mm.) did not fail.

One thermoscope which showed a deflection of 33 mm. did not break down. At the end of 15 days this was taken off the testing board and again examined for rectifying effect, when it was found that it no longer gave a deflection of 33 mm., but one of $\pm$ 4 mm., *i. e.*, the galvanometer coil moved slowly back and forth 4 mm. on either side of the zero.

In spite of this anomaly the statistical results of the experiment seemed to confirm the usefulness of the hypothesis: that a rectifying effect of the thermoscopes was the cause of their failure on an A.C. circuit. However, another experiment showed that the explanation was not so simple as it first appeared.

XVII.

In the regular method of making thermoscopes, pieces of copper wire were fused to the strips of sterling silver sulphide, but a number were made up with silver wire leads, the notion being that there would be no rectifying effect with them. But when these were tested they were found to give very large deflections on the galvanometer. On the other hand, no thermoscope made up with silver wire leads has ever broken down on an A.C. circuit. In the following table the results of an experiment on 5 silver-wired thermoscopes are given. These were first tested with the apparatus of Fig. 6, then put on the 20-volt A.C. testing

board for 15 days, after which they were again tested for galvanometer deflections.

Thermoscope Letter	Galvanometer Deflections Original	After 15 days.
A	52	±2
B	30	±2
C	45	±2
D	250	25
E	30	±2

Thus in the case of four thermoscopes the rectifying effect became zero in 15 days and is reduced 90 percent in the case of one.

A hypothesis may now be formed as to why in some cases thermoscopes with copper wire connections lose their rectifying effect in time, as found in Experiment XVI. In the process of fusing the wires to the sulphide strip the sulphide in contact with the copper wire is reduced to metallic silver, so that we have in effect silver electrodes. *The truth of this explanation has not been tested.*

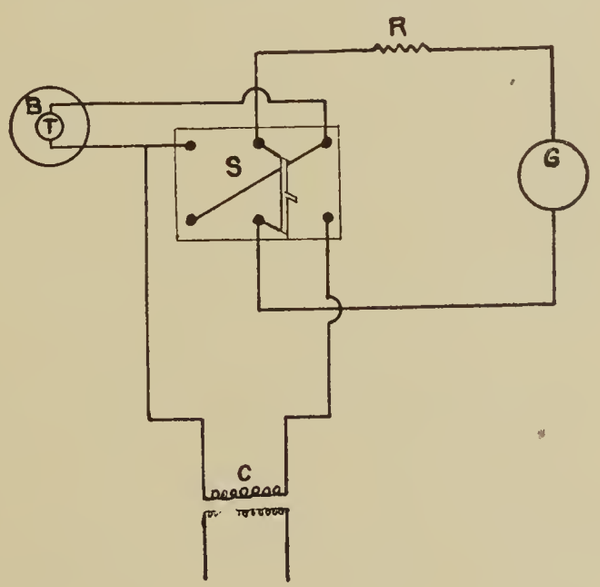


FIG 6.

XVIII.

In describing the diagram of Fig. 6 an oil bath was mentioned, as well as a switch for connecting the thermoscope to the galvanometer. Those parts of the apparatus were used in this experiment.

A thermoscope with silver wires fused to the sterling silver sulphide strip was made up, and the rectifying effect determined

under various temperature conditions. The observations made seem worth recording. Throughout this experiment the value of R was 100,000 ohms. The letters heading the columns in the table have the following meanings:

T=Temperature of oil bath in Centigrade degrees.
V=Transformer circuit e.m.f. in volts.
Gt=Galvanometer reading with alternating current. The readings are marked + or — according as the deflection was to the right or left respectively. When not marked, + is understood.
Gb=Galvanometer reading when the thermoscope was directly connected to the galvanometer. This when observed was done immediately after reading the corresponding value of Gt.

TABLE I.

T	V	Gt	Gb	Remarks
26	20	3		Transformer circuit only closed long enough to take reading.
36	20	2		
43	20	5	—4	Gt readings are mean values.
49	20	21	—5	
65	20	27	—8	
76	20	51	—7	
87.5	20	77	—2	
94.6	20	220	+1	
98.0	5	160	+1	
102.4	5	165	+1	
104.2	5	160	...	
105.5	5	0	0	
100.2	5	0	0	
95.0	5	0	0	
92.4	10	0	0	
91.2	10	0	0	
89.0	10	1	0	
82	10	1	0	
81.4	20	3	...	
80.0	20	120	0	
76.8	20	137	...	
92.0	5	40	...	Transformer circuit left closed.
100.0	5	40	...	
105.0	5	53	...	
105.4	5	45	...	
105.5	5	0	...	1.40 P. M.
87.3	20	0	...	2.50 P. M.
84.4	20	1	...	3.20 P. M.
83.4	20	110	...	
102.4	5	34	...	3.33 P. M.
103.6	5	30	...	3.45 P. M.
104.8	5	30	...	3.55 P. M.
105.0	5	40	...	3.58 P. M.
105.4	5	0	...	3.59 P. M.

The readings Gt are, as nearly as could be judged, the mean value of the deflections, for the direct current is not constant, the galvanometer coil generally traveling slowly back and forth over a short space, though sometimes the deflection is steady for a time. All the readings taken are not given, as they would make the table needlessly large.

There are several interesting observations to be noted in this table. In the first place, there was apparently no permanent rectifying effect at the beginning of the experiment, the galvanometer showing that the current changed slowly in direction. As the temperature rose, however, rectifications became evident. Then the direct current increased with rise of temperature till it suddenly disappeared at about 105°. This critical point was checked twice, with rising temperature.

On cooling, the rectifying effect did not appear again until the temperature had dropped to 89°. The first time this was tried no record of the time of cooling was kept, but it was certainly short, as the heating coil in the oil was cut out completely. The next time, however, in cooling from 105.5° to 84.4°, when the rectifying effect again appeared, the time of cooling was 100 minutes, or a rate of only 0.2° per minute.

It is also interesting to note that throughout the experiment there seemed to be a diminution of the rectifying effect at all temperatures, just as any thermoscope with silver wire leads loses its rectifying effect in an A.C. circuit.

Turning now to the temperature-resistance curve in Fig. 5 for the sterling silver sulphide thermoscope, it is seen that the sudden change in resistance with rising temperature occurs at 104°. This suggests some relation between the critical temperature of the resistance curve and that of the disappearance of rectification.

It was pointed out that the critical temperature of the resistance curve obtained when the sulphide is cooling is not the same as when heating, and it seems probable that here also there is a correlation with the rectifying effect.

The few readings of Gb taken are also interesting. Remembering that when the switch is thrown over the connection to the galvanometer is reversed, it is seen that at first the direction of the current generated by the thermoscope is the same as the

direct current obtained from the alternating current, but this is reversed at a higher temperature.

The relation, if any, between the current generated by the thermoscope itself and the current obtained from the alternating current is not clear. This led to another experiment.

XIX.

The apparatus of Fig. 6 was used, but the oil bath was omitted. R had a value of 10,000 ohms, and the transformer e. m. f. was 20 volts. The thermoscope was made of a sterling silver sulphide strip with silver wire leads. These observations were made:

Deflection with A. C. current — 25 mm.
Deflection by Thermoscope as battery — 5 mm., therefore, in opposite direction to the A. C. — D. C. current.

The thermoscope was then put in a 6-volt D.C. circuit so as to reverse its polarity (see Experiment IV), and when tested with the galvanometer gave a deflection of +5 mm.

Deflection with A.C. current —35 mm., therefore, in the same direction as before but greater by just the amount of change in deflection produced by charging with the D.C. current.

The thermoscope was now put in the 6-volt D.C. circuit again for a few minutes, but with the contacts reversed. When tested with the galvanometer a deflection of —25 mm. was obtained.

Deflection in A.C. circuit —35 mm., diminishing after 20 minutes to —26 mm.

Deflection by thermoscope as battery —6 mm.

Thus the thermoscope has finally recovered its original condition.

It was next charged in the D.C. circuit until acting as battery it gave a deflection of +7 mm. It was then left in the galvanometer circuit, when it was observed to discharge slowly, finally passing zero and giving a deflection of —2 mm.

Put again in the A.C. circuit and left for 10 minutes it gave a deflection of —30 mm., and as battery a deflection of —5 mm. Left in the galvanometer circuit for several hours this deflection slowly diminished to zero.

XX.

It would obviously be interesting to make an experiment on the variation of the rectifying effect with temperature in the case of a thermoscope made of pure silver sulphide. This was tried once, but the results were altogether unsatisfactory, as the rectifying effect was so small at all temperatures. Whether or not this is due to the presence of impurities in the sulphide being a necessary condition for rectification has not been determined.

It would also be interesting to study the behaviour of other solid electrolytes with the apparatus of Fig. 6. A few experiments were made in this way by making cells with graphite discs as electrodes, coating one of these with a mixture of oxides and water, drying and then clamping the graphite discs together. Tested in this way the rectifying effect was observed with the following oxides: cupric, ferric, lead (peroxide), cobalt, nickel, mercuric and with silicon carbide. It is not desired, however, to lay any stress on these observations, since the conditions are imperfectly known, as, for example, whether or not the electrolytes were pure or even quite dry.

It is fully realized that some apology is necessary for the presentation of these notes, representing as they do a quantity of undigested observations and a number of incomplete investigations. It must be remembered, however, that the experiments were only incidental to work on the development of a marketable thermoscope, and that in a merely commercial laboratory commercial considerations must predominate. Nevertheless, some conclusions which seem worth while may be drawn from the notes.

CONCLUSIONS.

1. Silver sulphide is a solid electrolyte well worthy of study, since it lends itself admirably to experiments having for their object research on the properties of electrolytes of this class.

2. The temperature-resistance curve of silver sulphide shows a critical point at a certain temperature, but this is not the same on the heating and cooling curves.

3. The temperature-resistance curve of silver sulphide is strongly affected by impurities. Thus pure silver sulphide gives a critical point with rising temperature at 170°, sulphide from an

alloy containing 0.5 percent copper has a critical temperature of 163°, and that made from the 7.5 percent allow a critical temperature of 104°.

In this relation it is interesting to note that Northrup has found a critical temperature for alundum at 1100°.[3]

4. Silver-silver sulphide and copper-silver sulphide form thermoelectric couples, the effect of which must be looked for in experimental work on silver sulphide.

5. Even very slight chemical reduction in a mass of silver sulphide has a great effect on its electrical resistivity.

6. Lack of homogeneity in the sulphide made from silver-copper alloy has an important influence on its electrical properties. The resistivity is greatly affected, and probably also other characteristics such as the thermoelectric and rectifying effects. Much of the experimental work on this point has not been mentioned because it is of too incomplete a character, but the observations made are such as to warrant a warning. This would probably explain certain anomalies which may be found in the case of mixed sulphides. These anomalies are comparable to the case of alloys where there may be a "false resistance" due to thermoelectric effects, as pointed out by J. J. Thomson.[4]

7. Electrolysis may occur in a Cu — $Ag_2S + Cu_2S$ — Cu cell in a 25-cycle A.C. circuit, with the result that the cell is eventually short-circuited. On the other hand, if silver electrodes are used the cell is not short-circuited.

8. Electrolysis in the Cu — $Ag_2S + Cu_2S$ — Cu cell is probably due to a persistent rectifying effect. This rectifying effect is very marked in a cell where one copper electrode is coated with cupric oxide.

9. A rectifying effect may also be shown with an Ag — $Ag_2S + Cu_2S$ — Ag cell, but after being in an A.C. circuit for some time this disappears.

10. In the Ag — $Ag_2S + Cu_2S$ — Ag cell showing a rectifying effect there is a critical temperature at which this disappears on heating, and a different critical temperature at which it reappears on cooling. These critical temperatures may be cor-

[3] Metallurgical and Chemical Engineering, Vol. XII, pages 126 *et seq*, February, 1914.

[4] "The Corpuscular Theory of Matter," p. 59 (Scribners) 1907.

related with the critical points of the temperature-resistance curves. Study of this phenomenon might throw some light on the nature of conduction in solid compounds, whether this is electrolytic or electronic or both.

The FitzGerald Laboratories,
Niagara Falls, N. Y.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

POLARIZATION SINGLE POTENTIALS.

By Claude N. Hitchcock.

In a very interesting paper upon the decomposition of water, which appeared in a previous volume of the Transactions of this Society, J. W. Richards[1] obtained decomposition at an impressed electromotive force of only 1.15 volts instead of 1.67 volts, the value generally accepted for the decomposition point of water. This abnormal result was attained by the use of platinum electrodes differing greatly in size.

The experiments which follow were undertaken for the purpose of determining the potential at each electrode in such cases of decomposition of electrolytes below the normal decomposition point.

A description of the apparatus used and a word as to the mode of procedure will be considered before going into a detailed account of the experimental work.

Fig. 1 shows a diagram of the apparatus. A constant potential of ten volts was applied to a nichrome wire resistance coil *R*, from which any desired potential up to ten volts could be picked off by means of sliding contacts. By following out the connections in the above diagram the system will be easily understood. Key *K* requires a little explanation. This is a combination of a double-pole line switch and a short-circuit galvanometer key. With the lever in normal position, *m* and *m'* are connected to *n* and *n'* respectively by means of two side levers not shown, and *d* is connected by a top contact to *c*. When the lever is pressed down the electrolyzing circuit is broken and *c* is connected by a bottom contact to *b*.

The voltmeter used was an accurately calibrated instrument, from which readings could be obtained in millivolts. A milli-

[1] Vol. 4, p. 120 (1903).

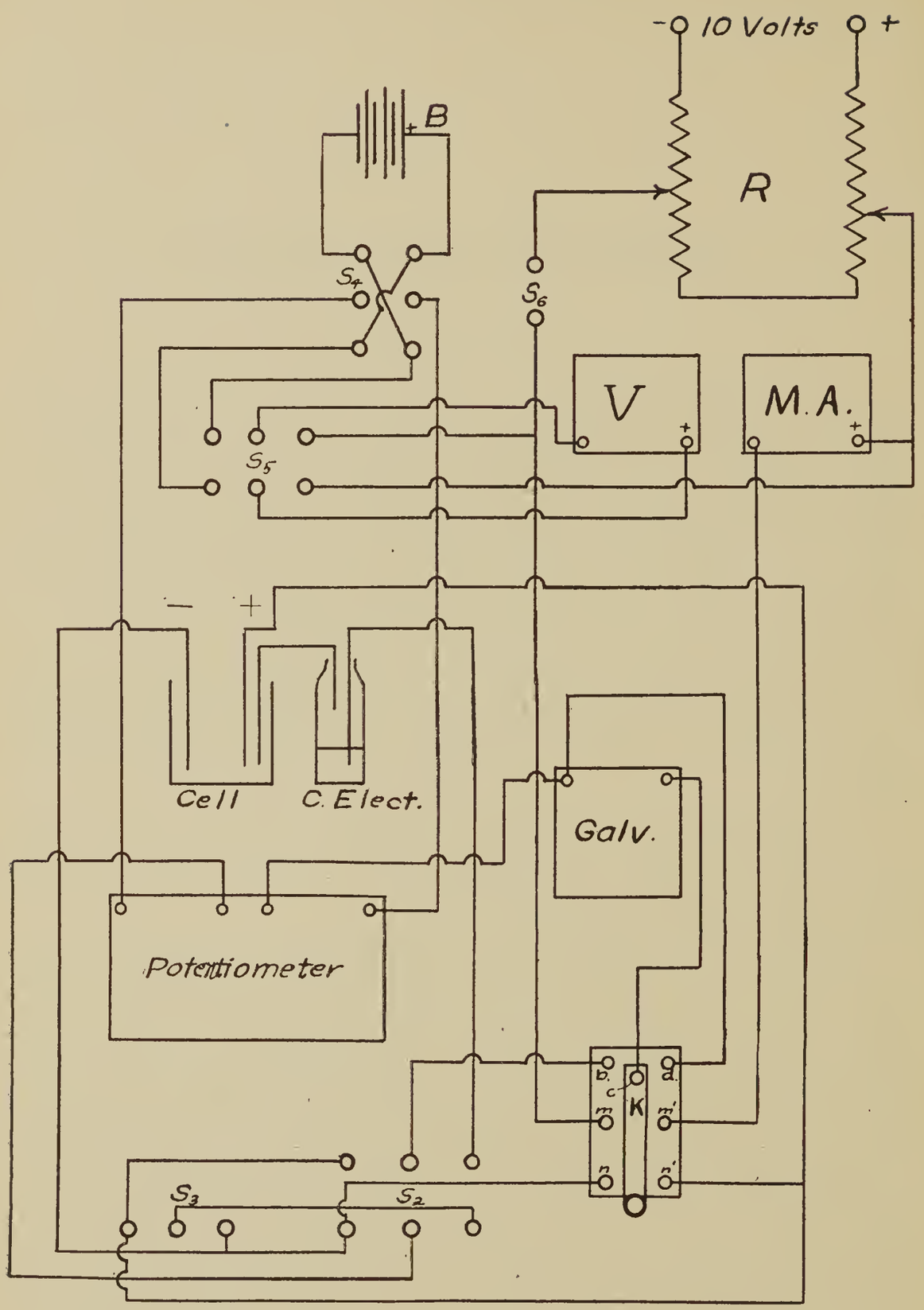


FIG. 1.

ammeter reading to hundredths of a milliampere was used, not so much to read exact values of current (for these experiments were not intended to deal with residual currents) as to indicate

when that point in the experiment had been reached at which an appreciable current flowed through the cell.

Measurement of instantaneous values of polarization was accomplished with a potentiometer, this being a more accurate device than a millivoltmeter, as it drew from the system no current that would tend to destroy the maximum values of the counter electromotive forces. The calomel electrode had a potential of —0.56 volt, and it was frequently compared, during the series of experiments in which it was used, with another reserved for the purpose.

To manipulate the foregoing apparatus the cell and normal electrode were connected to the system as shown. To read total potential the switch S_3 was left open and switch S_2 was thrown to the left. By tapping the key K and adjusting the potentiometer, the galvanometer, an instrument sensitive to one micro-ampere, showed when the total potential was equal to that recorded by the potentiometer. In like manner the single potential of the cathode was found with switches S_2 and S_3 thrown to the right; and of the anode with S_2 thrown to the right and S_3 to the left. After obtaining initial values of total, cathode and anode potential, switch S_6 was closed and the sliding contacts arranged on R to pick off the voltage desired. The minimum voltage impressed on the cell was 0.2 volt, and from this starting point the electromotive force was increased at the rate of 0.1 volt per minute in increments of 0.2 volt, except around the decomposition point, where 0.1 volt increments were used.

The electrolyte used in most of the experiments was a normal sulphuric acid solution, made up from c. p. acid and distilled water. The solution was boiled to remove dissolved gases, cooled in a closed flask, and re-standardized with air-free water. Solutions used, differing from the above, will be noted.

Platinum electrodes were employed in all experiments. The regular procedure was to heat the electrodes to a red heat and plunge them into the electrolyte just before the experiment began.

Before attempting a study of electrolysis with electrodes of unequal size, it was deemed best to secure data under the standard conditions of equal electrodes.

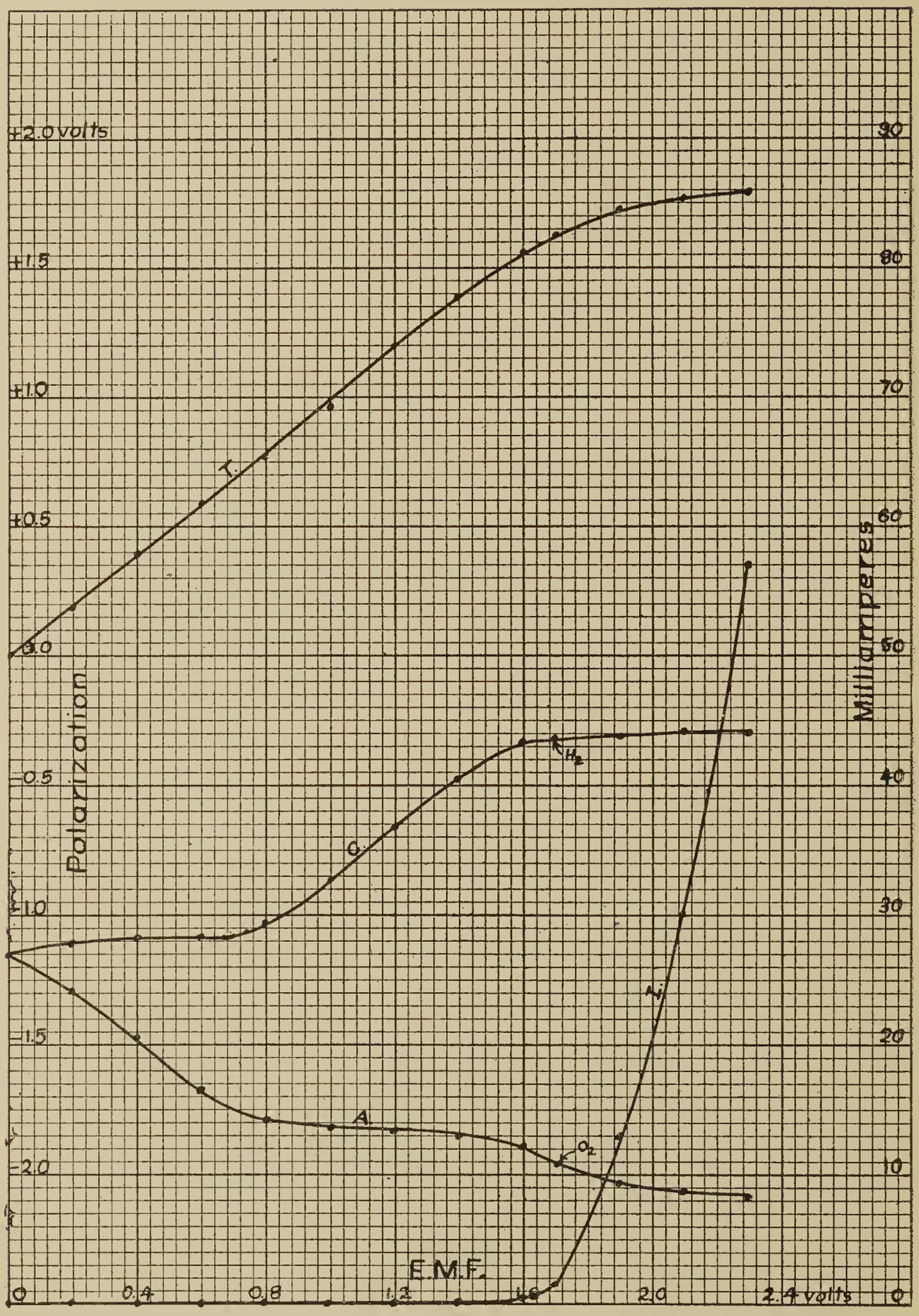

+2.0 volts
+1.5
+1.0
+0.5
0.0
-0.5
-1.0
-1.5
-2.0
Polarization
T.
H2
C.
A.
O2
Milliamperes
90
80
70
60
50
40
30
20
10
0
E.M.F.
0
0.4
0.8
1.2
1.6
2.0
2.4 volts

PLATE I.

EXPERIMENTS WITH ELECTRODES OF EQUAL SIZE.

No. 1.

Two platinum electrodes, each one centimeter square, were placed one centimeter apart in a cell holding 60 c.c. of electrolyte. The latter had stood exposed to the air for a short time before the experiment began, no precautions being taken to prevent absorption of air by the solution. Table I at the end of this paper gives the data secured, from which the curves of Plate I have been plotted. The curves plotted with total polarization as ordinates and impressed electromotive force as abscissae are denoted by T with a subscript corresponding to the number of the curve. The curves drawn with impressed voltage as abscissae and electrode potentials for ordinates are marked C for the cathode and A for the anode. Current Curves I are plotted with the same abscissae, and current values for ordinates. Current values plotted are the average that flowed during the two minute intervals between increments of electromotive force.

An inspection of this plate at once shows that the cathode curve is peculiar. Although the maximum change in potential of each electrode is about the same, up to an impressed electromotive force of 0.6 volt, the cathode still has almost its initial potential, while the potential of the anode has changed over 0.5 volt. If it be assumed (and there seems to be no escape from the assumption) that the successive changes in the potential of the anode are caused by the deposition of oxygen by that momentary current which is observed to flow every time the voltage is increased, it follows that twice as much hydrogen by volume must have been deposited on the cathode. Since little change in potential resulted, this hydrogen must have been removed as fast as deposited, and suspicion falls upon the air contained in the solution as being the depolarizing agent.

No. 2.

Another sample of the same electrolyte was, therefore, boiled to remove the dissolved gases and kept covered with a layer of kerosene during cooling and subsequent use. The results are shown in Table II and Curve I, Plate II.

Comparing the curves for this test with those for Experiment I,

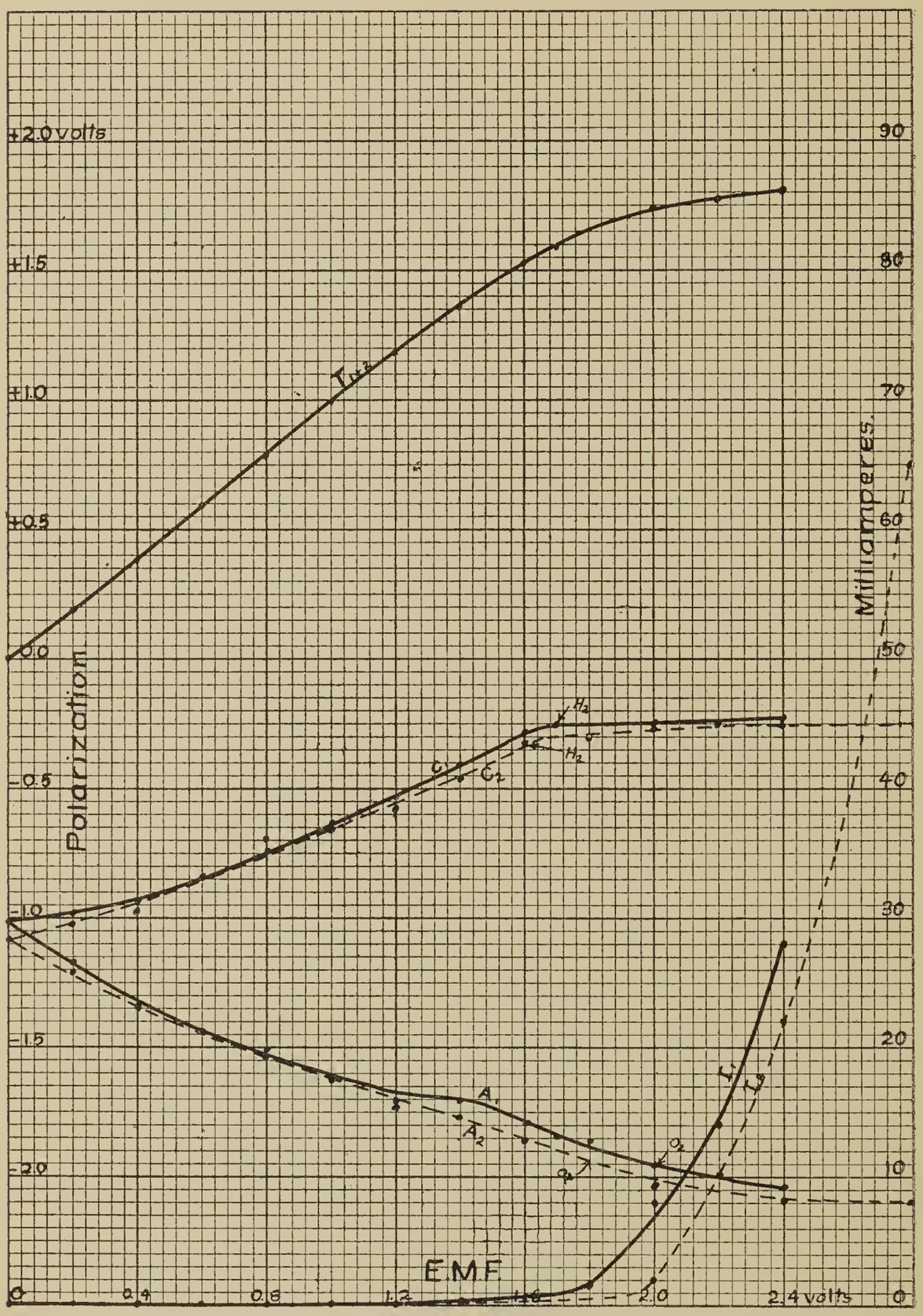


PLATE II.

it is at once evident that different conditions existed. Instead of remaining constant for the first few increments of voltage as before, the cathode potential here begins to rise as soon as elec-

tromotive force is applied to the cell. Taking into account the precautions used for exclusion of air, it is reasonable to conclude from the smaller degree of cathode depolarization observed in this experiment that where oxygen is dissolved in the electrolyte, owing to contact of the electrolyte with the air, depolarization results. That all oxygen had not been expelled from the electrolyte in the present case, however, seems probable, for the slight downward curvature of the cathode potential line suggests that some small depolarizing factor was still present. Before going to the next experiment, in which further elimination of dissolved oxygen was tried, it might be noted that the evolution of oxygen in this experiment occurred after hydrogen had begun to come off, due, no doubt, to the greater solubility of oxygen in water.

No. 3.

In this experiment the solution was made up as in the one before, but, instead of covering the electrolyte with kerosene, the cell and calomel electrode were placed under a bell jar and the experiment carried out under a reduced pressure of one-third of an atmosphere. This helped materially in removing the air dissolved in the electrolyte (see Table III and Curve II, Plate II). Not only was dissolved oxygen drawn out of the solution, but the appearance of gas at both electrodes at lower applied voltages than in experiment *No. 2* indicates that reduction of pressure removed some of the oxygen deposited at the anode which otherwise might have diffused over to the cathode, causing depolarization there. At any rate, depolarization is observed to occur at a constant rate at both electrodes. Both electrode potential curves approximate straight lines, a result not obtained by either of the foregoing experiments.

It is to be noted from the results of experiments *Nos. 2* and *3* that, altho the potential curves of cathode and anode vary considerably from each other in the two cases, still the total polarization curves for both coincide.

No. 4.

Finally, in order to add one more proof to the above conclusion on the depolarizing effect of dissolved oxygen, an experiment similar to *No. 1* was run, using a solution through which pure

oxygen had been bubbled for five hours. Table IV gives the data taken, which, when plotted, gave total and single potential curves coinciding exactly with those of Plate I. We can therefore conclude that on standing exposed to the air for a short time the electrolyte used in these experiments became practically saturated with oxygen.

EXPERIMENTS WITH UNEQUAL ELECTRODES.

Having become familiar with the relations that exist between anode and cathode polarization when the electrodes are of equal size, and having established the effect of dissolved oxygen on such polarization, experiments were next undertaken with electrodes of unequal size.

No. 5.

A cell was arranged with a cathode one centimeter square and an anode one hundred times as large. The electrodes were placed one centimeter apart in a normal sulphuric acid solution (see Table V and Curve I, Plate III). In agreement with Richards' results,[2] gas was observed to come off from the cathode at 1.1 volts. From the presence of oxygen in the solution, however, depolarization of the cathode should occur as in experiment *No. 1,* yet the curves here appear more like those of experiment *No. 2.* The reason for this must be sought in the use of the large anode. Now, the current density at the cathode is one hundred times as great as at the anode. Two hundred volumes of hydrogen are discharged at the cathode per square centimeter for every volume of oxygen discharged per square centimeter at the anode, so that, even though the normal amount of oxygen in the solution did tend to depolarize the cathode as in experiment *No. 1,* still, with such large quantities of hydrogen a similar effect could not be produced. This large quantity of hydrogen distributed over a small area also accounts for the early saturation of the electrolyte around the electrode to such an extent that hydrogen appears as bubbles of gas. The opposite conditions at the anode are indicated by the slower rate of polarizing and the tardy evolution of oxygen.

At low values of applied voltage, larger current now flows

[2] Trans. Am. Electrochemical Society, 4, 120 (1903).

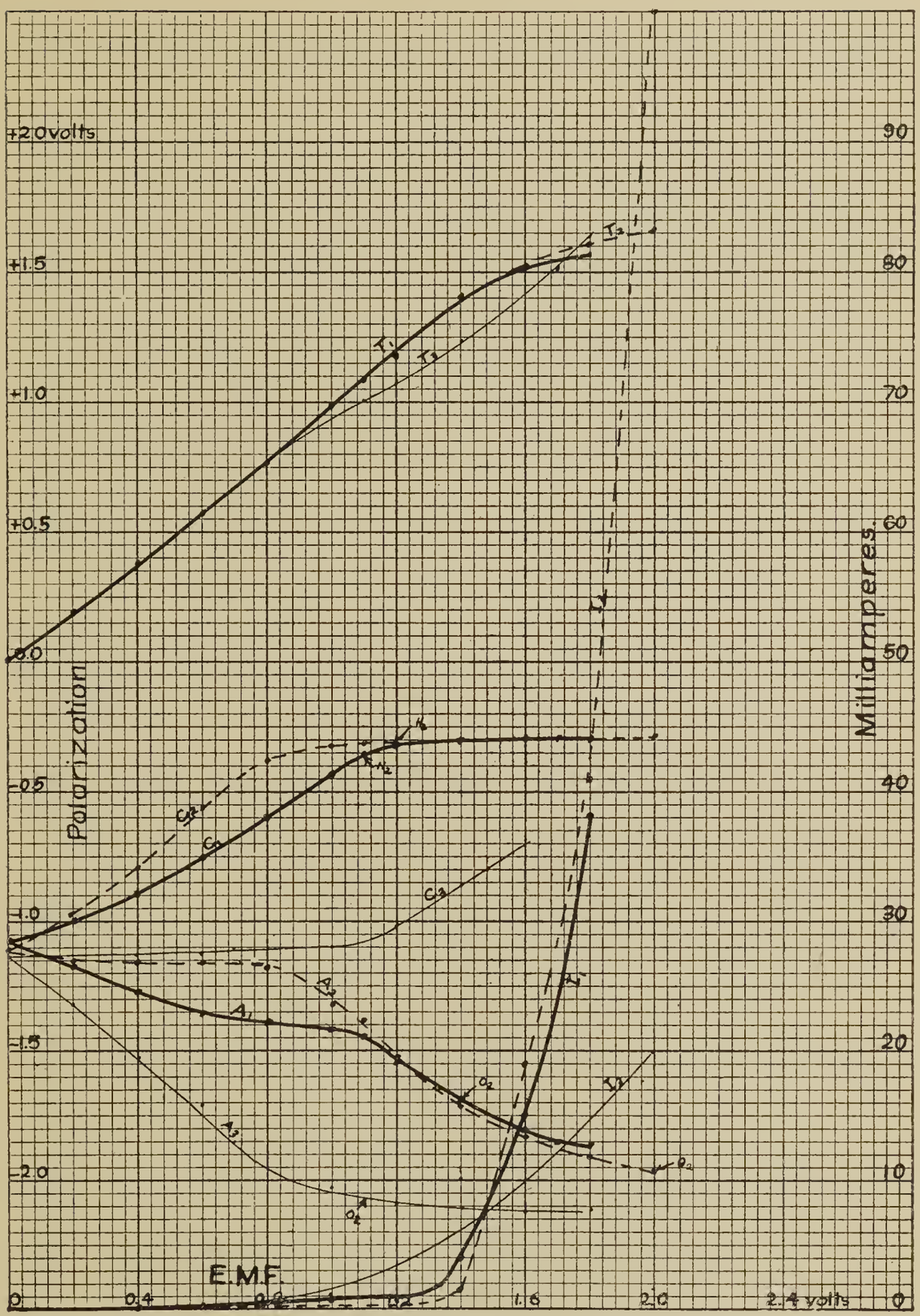


PLATE III.

than in the experiments with electrodes of equal size. The large amount of electrolyte in contact with the oxygen film at the anode dissolves the gas there with such facility that an appreciable

current must flow through the cell to maintain even the lower degree of anode polarization observed.

No. 6.

This was a repetition of experiment *No. 5,* with the same solution. The electrodes were, however, removed, heated and replaced in the cell before use. Table VI and Curve II, Plate III, show the results.

A comparison with Curve I on the same plate shows that, whereas in the previous case there were evidences of depolarization occurring at the cathode, in this case there is practically none, for the anode potential remains constant up to an impressed E. M. F. of 0.8 volt, and only changes then because the potential of the cathode has approached close to its limit. It seems likely that this condition is due to complete removal of the oxygen in the solution by the hydrogen evolved during experiment *No. 5.* With the cathode thus free to be polarized without hindrance, it follows that, up to saturation of the electrolyte around the cathode with hydrogen, almost the entire polarization of the cell will occur at this terminal.

No. 7.

In this experiment the relative sizes of anode and cathode were reversed, causing a reversal of the characteristics of the anode and cathode curves from those of experiment *No. 6* (see Table VII and Curve III, Plate III). This experiment was performed with a fresh solution, so that the depolarizing effects of dissolved oxygen may again be expected; and, indeed, inspection of the curves plotted shows that this oxygen, together with the dissolving of hydrogen from the cathode by the electrolyte, served to eliminate entirely even that small polarization which might be expected to occur with so large a cathode. The cathode potential remains constant up to an impressed E. M. F. of 0.9 volt. This forces the polarization of the cell wholly on the small anode, with the result that the latter very soon reaches the discharge potential of oxygen, about —2.0 volts, and oxygen appears at an impressed electromotive force of 1.1 volts.

These latter experiments show very plainly that if for any reason the potential of one electrode lags behind its normal course, the potential of the other must change by a corresponding

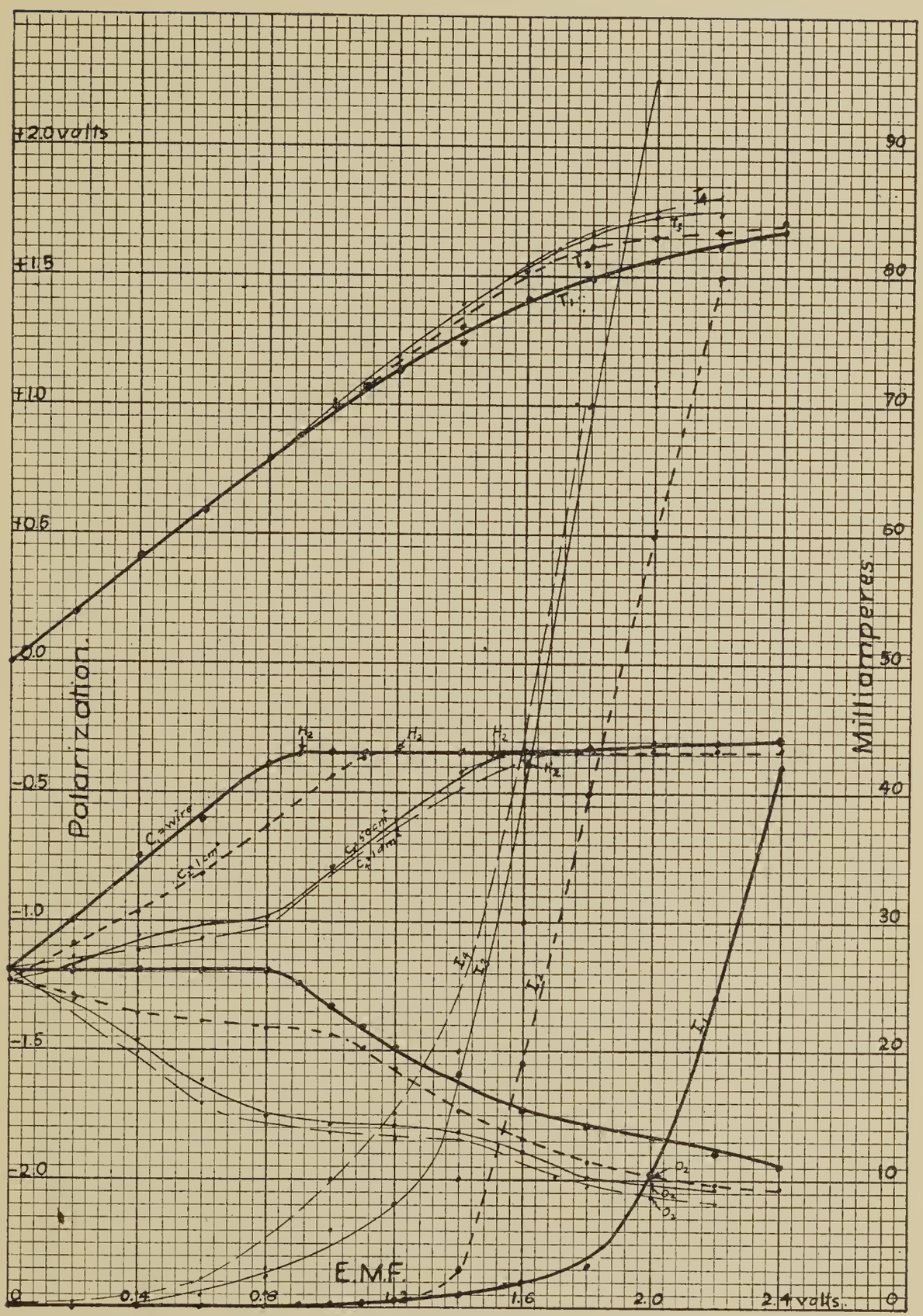


PLATE IV.

amount to make up for it. In all cases the total polarization must equal the sum of the separate electrode potentials.

EXPERIMENTS WITH CATHODES OF INCREASING SIZE.

It was found in the earlier experiments that hydrogen appeared at the cathode, as Richards stated, at values of impressed electromotive force far below the generally accepted decomposition point, 1.67 volts. To prove that the degree of lowering of decomposition point varies as the difference in electrode areas, the following experiments were performed. A platinum anode of constant size, one decimeter square, and a platinum cathode that varied from a wire 6.0 millimeters long by 0.75 millimeter in diameter to a sheet of platinum equal in area to the anode were employed. A fresh acid solution was used for each of the four experiments made, and the electrodes were heated and quenched each time, as usual. The data in Tables VIII–XI have all been plotted on Plate IV, to better disclose the results of the experiments.

It is apparent that in each case the potential of the cathode is —0.35 volt at the points where hydrogen is given off. This occurs regularly, and seems to be independent of the value of the impressed electromotive force. Current densities in milliamperes per square centimeter, at which hydrogen was first evolved at the cathodes from sulphuric acid, are found to be 1.5, 0.7, 0.3 and 0.25. Richards says:[3] "From a great number of experiments the conclusion is evident that current density at the electrodes is the prime factor in determining visible evolution of gas. * * * Measurements of current and area show that approximately 5 micro-amperes per square millimeter are necessary for the visible evolution of gas."

While the above statement is doubtless true for the conditions of Professor Richards' experiments, where the electrodes were a considerable distance apart and connection between them was made by a capillary tube, it requires modification when the electrodes are near together and in a relatively large volume of electrolyte which is exposed to the air, as is usually the case in practical electrolysis. Since a goodly share of the current flowing is used up in counterbalancing the effect of dissolved oxygen, it would perhaps be better to say that the gas evolution point is reached when the current density, minus the current per unit area used in off-setting depolarizing forces, has reached

[3] *Loc. cit.*

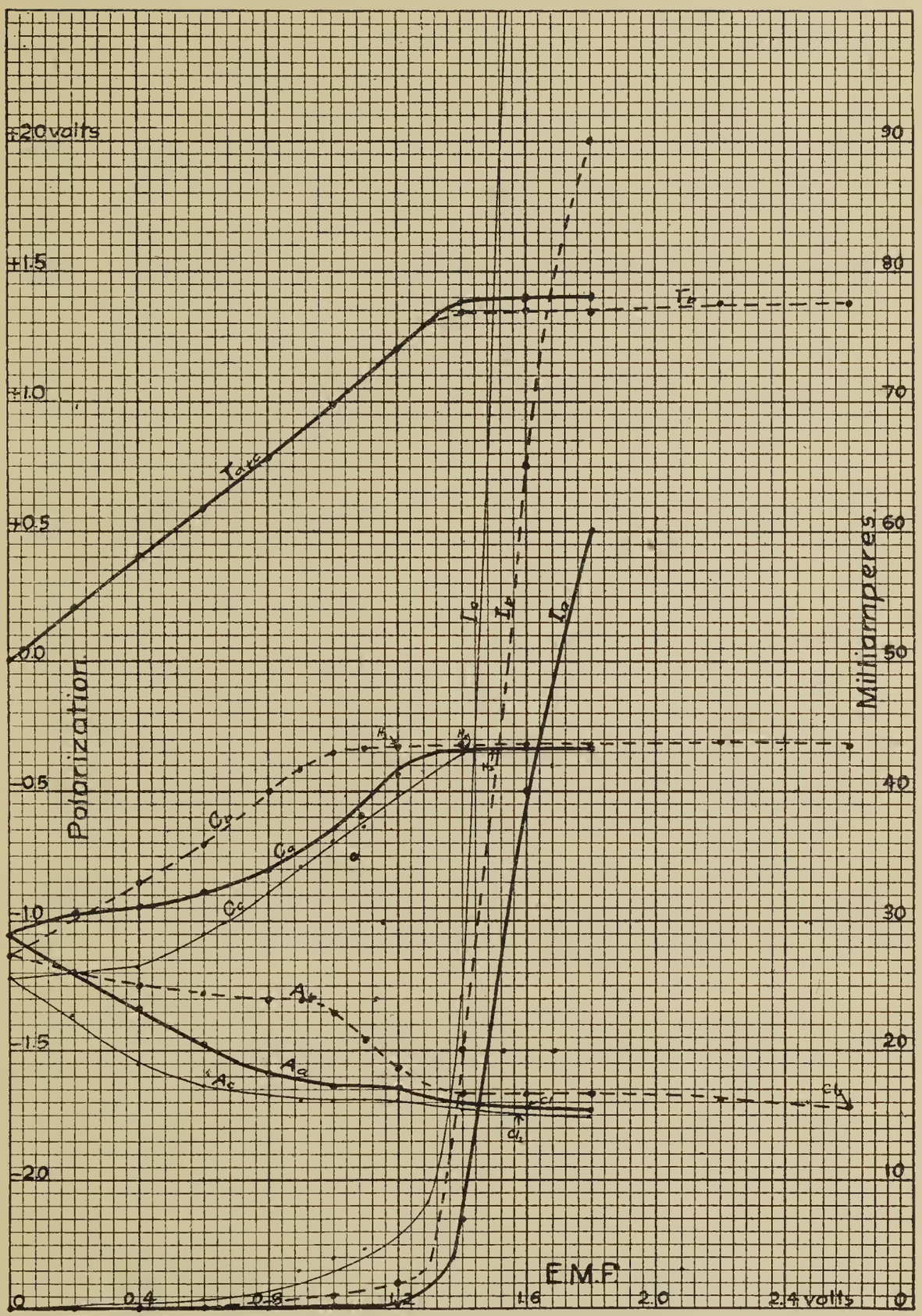


PLATE V.

some definite value. The evolution of hydrogen from normal hydrochloric acid required much higher densities, 7.0 and 2.0 milliamperes per square centimeter, than in sulphuric acid. This

is explained by the greater solubility of chlorine, and consequently a more rapid removal of hydrogen from the cathode than was possible by the less soluble oxygen.

It is evident that the point at which a particular gas will be evolved at an electrode cannot in general be exactly defined either in terms of the impressed electromotive force or of the current density, but it can be expressed in terms of electrode potential. Whenever the cathode potential has risen to a particular value (in these experiments —0.35 volt) which may be called the discharge potential of hydrogen, evolution of that gas will occur, irrespective of the value of the electromotive force or the current density at that time. Similarly when the anode potential has fallen to the definite value of the discharge potential of oxygen, that gas will appear.

Variation of impressed electromotive force for gas evolution points was secured between 0.9 volt and 1.67 volts, using the electrodes described. Had there been greater differences in electrode size, it no doubt would have been shown that decomposition may take place at practically any voltage, provided the proper electrodes are employed.

It is of further interest to note the increase in current for a given voltage, below the decomposition point, as the cathode area is increased. With very large electrodes in an acid solution it would be possible to pass large currents through a cell and still obtain no visible decomposition of the electrolyte.

EXPERIMENTS USING HYDROCHLORIC ACID FOR THE ELECTROLYTE.

After the above work with sulphuric acid solution, three sets of data were obtained on cells filled with normal hydrochloric acid (not air free). The platinum electrodes were of the following dimensions:

Experiment	Cathode	Anode
a	1 square centimeter.	1 square centimeter.
b	1 square centimeter.	1 square decimeter.
c	1 square decimeter.	1 square centimeter.

From Tables XII to XIV and Plate V, it is seen that the results were very similar to those obtained with sulphuric acid. Again, hydrogen appears when the cathode reaches a potential of —0.33 volt, no matter what the size of the electrode or what the im-

pressed voltage. The same occurrence is noted at the anode, where chlorine appears at —1.7 volts.

That chlorine is a very active depolarizer is shown by the results of experiment *c*. A large quantity of chlorine is deposited over a small anode area in this case, and is readily dissolved by the electrolyte and distributed throughout the cell. Coming in contact with the cathode, where the hydrogen concentration is small, it removes this so rapidly that the very large current shown is necessary to polarize the cathode at all. The same result is not obtainable with the other arrangements of electrodes, since with them there is not such free access of the chlorine to the cathode as in experiment *c*.

It will be noted that the initial potentials of the platinum electrodes in the three experiments were not the same. This was due to absorption of air by the electrolyte, the solution longest exposed giving the lowest initial potential.

ON THE USE OF PLATINUM ELECTRODES.

There has been much question as to advisability of using platinum for electrodes in a decomposition cell where gas is evolved. It has been claimed that, owing to the remarkable occluding powers of platinum for hydrogen and other gases, the potential of such an electrode must vary and, in varying, subject experimental work in which they are employed to a considerable degree of inaccuracy.

Several experiments were tried in order to determine if the potential of such electrodes changed as much as has been claimed.

No. 8.

A cell with platinum electrodes one centimeter square was set up and 0.2 volt impressed over its terminals. At intervals of several minutes readings were obtained of total, cathode and anode polarization. At the end of twenty minutes the voltage was raised to 0.8 volt, readings obtained as before, and the process repeated again at 1.4 volts. Table XV shows that the electrode potentials change very little with time, surely not enough to introduce serious errors into decomposition experiments. Table XVI shows the same results for a cell fitted with a small cathode

and a large anode. While these results may appear unexpected, still, if the time taken for the electrodes to reach their final potential for any value of impressed electromotive force is considered, the above will not appear extraordinary.

Experiment shows that with cells like those used it takes but ten seconds for an anode polarization of 0.7 volt to build up, and twenty-five seconds for the same polarization to appear at the cathode, both representing final potentials under the conditions imposed. Furthermore, the cathode polarization falls off almost the instant the electrolyzing circuit is broken, but the anode polarization decreases very slowly. Indeed, lifting the anode from the cell, rinsing, drying or even heating[4] it, does not materially alter the slow rate at which the anode potential returns to its value before use.

These observations point to the following conclusions: (*1*) In the case of the anode, polarization is almost entirely due to the oxygen saturated electrolyte around the electrode. The slowness of diffusion of oxygen, the small occlusive power of platinum for oxygen, and the slow decrease of polarization on open circuit, seem to indicate that a very large part of the anode polarization is accounted for by the concentration of oxygen in the solution rather than in the electrode. An extremely thin film of saturated electrolyte, such as is produced at the surface of the anode on closing the circuit, suffices to completely polarize the electrode for the given applied voltage. Since neither diffusion nor occlusion decreases this instantaneous concentration to a great extent, it is to be expected that the anode will show its final value of polarization very soon after pressure is applied to the cell. Continued application of electromotive force merely serves to increase the thickness of the oxygen-saturated film. The value of polarization depends on the maximum and minimum concentrations of oxygen in the electrolyte between the electrodes ($e = R.\ T.\ log.\frac{C}{C'}$ where C is the concentration of oxygen at the anode and C' the concentration of that part of the electrolyte containing the smallest amount of oxygen), so that it does not matter whether the film is one-thousandth of a millimeter thick or thicker, so long as C and C' remain the same. (*2*) At the cathode the concentration

[4] Transactions Am. Electrochemical Society, **4**, 122 (1903).

of the film of hydrogen-saturated electrolyte produced by the first surge of current is diminished by diffusion (large for hydrogen) and by the occlusion of the gas by the platinum electrode. A longer interval is consequently required to build up the cathode potential, and as soon as the building and maintaining force—the impressed electromotive force—is cut off, the concentration is rapidly lowered, a fact in accordance with the rapid decline of cathode potential when the circuit is opened. It is true that platinum will continue to absorb hydrogen over an extended period of time; the continued upward slope of the cathode polarization curves after hydrogen evolution in any of the plates shown confirms that, but it is very evident that the greater part of occlusion occurs in a very short time, to be followed by a period of occlusion where the rate of absorption is so low that the potential of the electrode may be considered practically constant.

CONCLUSIONS.

It conclusion it may be stated that:

a. Decomposition of water can be accomplished at any voltage with platinum electrodes, provided the latter are of the proper size.

b. The oxygen normally present in laboratory reagents is sufficient to produce marked depolarization at the cathode.

c. The single potential of each electrode so depends on that of the other that any change in one, due to disturbing influences, is counteracted by such a change in the other that, below the decomposition point, the sum of the separate electrode polarizations equals the total polarization, and this in turn equals (very nearly) the impressed electromotive force.

d. Any desired current may be passed thru an aqueous solution of sulphuric or hydrochloric acid without causing evolution of gas, provided the electrodes are made large enough.

e. The evolution of gas at the electrodes depends on the total current density minus that part of the current density neutralized by the action of depolarizing agents.

The writer's thanks are due Dr. O. P. Watts for many valuable suggestions received in the above work.

TABLE I.

Electrodes of equal size, one centimeter square.
Electrolysis of normal H_2SO_4.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.005	—1.152	—1.160
0.2	0.0	0.181	1.118	1.296
0.4	0.0	0.390	1.090	1.477
0.6	0.05	0.581	1.090	1.673
0.8	0.07	0.766	1.033	1.798
1.0	0.20	0.960	0.867	1.825
1.2	0.20	1.185	0.671	1.839
1.4	0.20	1.378	0.476	1.853
1.6	0.60	1.556	0.337	1.895
1.7*	1.50	1.626	0.323	1.950
1.9	13.00	1.723	0.309	2.034
2.1	30.00	1.765	0.295	2.061
2.3	57.00	1.793	0.295	2.090

* Evolution of gas at both electrodes.

TABLE II.

Electrodes of equal size, one centimeter square.
Normal H_2SO_4 electrolyte covered with kerosene.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.022	—1.022
0.2	0.0	0.182	0.980	1.176
0.4	0.0	0.378	0.938	1.344
0.6	0.0	0.588	0.840	1.442
0.8	0.0	0.784	0.742	1.512
1.0	0.05	0.994	0.644	1.624
1.2	0.10	1.178	0.532	1.709
1.4	0.15	1.359	0.464	1.709
1.6	0.70	1.527	0.280	1.792
1.7*	0.70	1.597	0.252	1.849
2.0†	8.00	1.738	0.252	1.961
2.2	14.00	1.764	0.252	1.989
2.4	28.00	1.805	0.238	2.044

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE III.

Electrodes of equal size, one centimeter square.
Electrolysis of normal H_2SO_4 in partial vacuum.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.087	—1.087
0.2	0.0	0.180	1.031	1.217
0.4	0.0	0.388	0.989	1.363
0.6	0.0	0.595	0.837	1.432
0.8	0.0	0.789	0.698	1.529
1.0	0.0	0.969	0.657	1.611
1.2	0.0	1.190	0.588	1.750
1.4	0.05	1.370	0.422	1.778
1.6*	0.30	1.522	0.338	1.861
1.8†	1.5	1.633	0.311	1.861
2.0	2.0	1.716	0.280	2.040
2.4	22.0	1.854	0.261	2.082
2.8	65.0	1.854	0.261	2.110

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE IV.

Electrodes of equal size, one centimeter square.
Normal H_2SO_4 saturated with oxygen.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.144	—1.144
0.2	0.0	0.181	1.116	1.311
0.4	0.0	0.375	1.088	1.477
0.6	0.0	0.612	1.061	1.671
0.8	0.1	0.764	1.033	1.783
1.0	0.2	0.986	0.838	1.825
1.2	0.25	1.168	0.643	1.811
1.4	0.3	1.361	0.477	1.811
1.6	0.6	1.530	0.338	1.866
1.7	1.0	1.612	0.338	1.950
2.0	6.0	1.710	0.338	2.006

Oxygen evolved at anode at 1.9 volts E. M. F.

TABLE V.

Cathode = 1 centimeter square. Anode = 1 decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.014	—1.074	—1.088
0.2	0.0	0.181	0.991	1.172
0.4	0.0	0.375	0.908	1.269
0.6	0.4	0.570	0.755	1.325
0.8	..	0.765	0.615	1.380
1.0	0.5	0.986	0.435	1.421
1.1*	..	1.085	0.352	1.449
1.2	..	1.182	0.324	1.546
1.4†	4.0	1.404	0.309	1.687
1.6	15.0	1.516	0.296	1.798
1.7	..	1.516	0.296	1.852
1.8	38.0	1.571	0.282	1.852

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE VI.

Cathode = 1 centimeter square. Anode = 1 decimeter square.
Repetition of No. 5 with same lot of electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.014	—1.116	—1.130
0.2	0.1	0.193	0.977	1.157
0.4	0.2	0.348	0.796	1.157
0.6	0.2	0.598	0.560	1.157
0.8	..	0.806	0.379	1.172
1.0	..	0.986	0.338	1.325
1.1	0.25	1.099	0.324	1.394
1.2*	0.25	1.210	0.324	1.533
1.4	1.5	1.405	0.310	1.713
1.6	19.0	1.501	0.296	1.825
1.8	41.0	1.600	0.296	1.909
2.0†	100.0	1.669	0.296	1.979

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE VII.

Cathode = 1 decimeter square. Anode = 1 centimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.136	—1.136
0.2	0.5	0.181	1.136	1.327
0.4	0.5	0.404	1.136	1.537
0.6	0.5	0.600	1.136	1.703
0.7	0.5	0.698	1.120	1.858
1.0	1.0	0.949	1.104	2.025
1.1†	1.5	1.018	1.062	2.080
1.2	3.0	1.073	1.021	2.109
1.4	10.0	1.241	0.867	2.109
1.6	..	1.505	0.685	2.122
1.8	..	1.637	0.616	2.136
2.0	20.0	....	....	....

† Evolution of oxygen at anode.

TABLE VIII.

Cathode—Wire: area = 14 square millimeters.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.189	—1.189
0.2	0.0	0.195	0.999	1.189
0.4	0.0	0.419	0.755	1.185
0.6	0.0	0.586	0.602	1.185
0.8	0.0	0.795	0.393	1.185
0.9*	0.1	0.879	0.351	1.230
1.0	0.2	0.991	0.345	1.328
1.1	0.25	1.073	0.337	1.411
1.2	0.30	1.130	0.337	1.482
1.4	1.0	1.242	0.337	1.592
1.6	2.0	1.410	0.337	1.732
1.8	3.2	1.492	0.329	1.791
2.0	10.6	1.562	0.309	1.842
2.2	24.0	1.619	0.309	1.899
2.4	42.0	1.673	0.295	1.955

* Evolution of hydrogen at cathode.

TABLE IX.

Cathode = 1 centimeter square. Anode = 1 decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.230	—1.230
0.2	0.0	0.181	1.091	1.286
0.4	0.1	0.396	0.964	1.355
0.6	0.15	0.572	0.811	1.384
0.8	0.15	0.795	0.630	1.411
1.0	0.15	0.991	0.435	1.439
1.1	0.50	0.130	0.365	1.495
1.2*	0.60	0.213	0.359	1.561
1.4	3.0	1.381	0.337	1.737
1.6	19.0	1.520	0.331	1.849
1.8	40.0	1.618	0.331	1.928
2.0†	60.0	1.646	0.337	1.983
2.2	80.0	1.672	0.337	2.010
2.4	120.0	1.701	0.337	2.039

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE X.

Cathode = 50 square centimeters. Anode = 1 decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.231	—1.231
0.2	0.0	0.209	1.118	1.313
0.4	0.2	0.404	1.063	1.468
0.6	1.0	0.600	1.007	1.620
0.8	2.5	0.809	0.979	1.760
1.0	6.0	1.019	0.783	1.788
1.2	8.0	1.186	0.610	1.788
1.4	10.0	1.395	0.420	1.816
1.5*	15.0	1.479	0.350	1.843
1.6	30.0	1.549	0.337	1.899
1.7	40.0	1.604	0.337	1.928
1.8	70.0	1.660	0.328	1.997
2.0†	200.0	1.730	0.328	2.010
2.2	280.0	1.730	0.328	2.039

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE XI.

Electrodes of equal size, one decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.174	—1.174
0.2	0.1	0.196	1.146	1.338
0.4	1.0	0.404	1.119	1.509
0.6	2.5	0.629	1.063	1.703
0.8	3.0	0.782	1.007	1.788
1.0	10.0	0.004	0.797	1.815
1.2	15.0	1.185	0.644	1.843
1.4	20.0	1.352	0.476	1.843
1.6*	25.0	1.549	0.365	1.871
1.7	30.0	1.619	0.337	1.955
1.8	35.0	1.673	0.337	2.025
2.0†	95.0	1.757	0.323	2.065
2.2	200.0	1.813	0.309	2.095

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE XII.

Electrodes of equal size, one centimeter square.
Normal HCl electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.059	—1.059
0.2	0.0	0.208	0.970	1.198
0.4	0.04	0.403	0.948	1.336
0.6	0.04	0.596	0.879	1.475
0.8	0.05	0.776	0.809	1.586
1.0	0.10	0.984	0.643	1.639
1.2	0.15	1.205	0.435	1.639
1.4*	7.00	1.370	0.338	1.709
1.6†	40.00	1.399	0.338	1.722
1.8	60.00	1.399	0.338	1.722

* Evolution of hydrogen at cathode.
† Evolution of chlorine at anode.

TABLE XIII.

Cathode = 1 centimeter square. Anode = 1 decimeter square.
Normal HCl electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.142	—1.142
0.2	0.0	0.199	1.976	1.184
0.4	0.0	0.374	1.851	1.253
0.6	0.0	0.569	1.712	1.281
0.8	0.0	0.804	1.505	1.309
0.9	0.0	0.901	1.422	1.309
1.0	0.5	1.010	1.366	1.364
1.1	1.0	1.093	1.338	1.461
1.2*	2.0	1.219	1.338	1.570
1.4	20.0	1.343	1.333	1.667
1.6	65.0	1.343	1.333	1.667
1.8	90.0	1.343	1.333	1.667
2.2	450.0	1.375	1.311	1.695
2.6†	...	1.375	1.338	1.723

* Evolution of hydrogen at cathode.
† Evolution of chlorine at anode.

TABLE XIV.

Cathode = 1 decimeter square. Anode = 1 centimeter square.
Normal HCl electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.225	—1.225
0.2	0.0	0.180	1.198	1.364
0.4	0.0	0.402	1.170	1.558
0.6	0.2	0.596	1.058	1.640
0.8	2.0	0.804	0.893	1.695
0.9	3.0	0.901	0.795	1.695
1.0	4.0	0.984	0.698	1.695
1.1	4.5	1.094	0.643	1.695
1.2	5.0	1.163	0.518	1.695
1.4	23.0	1.370	0.353	1.723
1.6	112.0	1.436	0.338	1.750
1.8	190.0	1.412	0.338	1.750

Evolution of hydrogen at cathode at 1.5 volts E. M. F.
Evolution of chlorine at anode at 1.58 volts E. M. F.

TABLE XV.

Data on constancy of platinum electrode potentials.
Electrodes of equal size, 1 centimeter square.

Time	Impressed E. M. F. Volts	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
Beginning	0.0	+0.000	—1.185	—1.185
½ min. later.....	0.2	+0.195	—1.149	—1.338
2 " "	0.2	+1.195	—1.144	—1.338
6 " "	0.2	+0.195	—1.135	—1.325
10 " "	0.2	+0.195	—1.135	—1.325
14 " "	0.2	+0.195	—1.116	—1.310
20 " "	0.2	+0.195	—1.116	—1.310
Impressed voltage was increased.				
½ min. later.....	0.8	—0.778	—0.977	—1.756
2 " "	0.8	—0.778	—0.977	—1.756
6 " "	0.8	—0.778	—0.977	—1.756
10 " "	0.8	—0.778	—0.977	—1.756
14. " "	0.8	—0.778	—0.963	—1.742
Impressed voltage was increased.				
½ min. later.....	1.4	+1.377	—0.379	—1.756
2 " "	1.4	+1.377	—0.379	—1.756
4 " "	1.4	+1.377	—0.379	—1.756
10 " "	1.4	+1.405	—0.366	—1.756
20 " "	1.4	+1.390	—0.366	—1.756

TABLE XVI.

Data on constancy of platinum electrode potentials.
Cathode, 1 centimeter square. Anode, 1 decimeter square.

Time	Impressed E. M. F. Volts	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
Beginning	0.0	+0.000	—1.170	—1.170
½ min. later.....	0.2	0.180	1.073	1.253
5 " "	0.2	0.180	1.059	1.253
10 " "	0.2	0.193	1.059	1.253
15 " "	0.2	0.193	1.059	1.253
20 " "	0.2	0.193	1.059	1.253
Impressed voltage was increased.				
½ min. later.....	0.6	+0.595	—0.795	—1.363
5 " "	0.6	0.595	0.782	1.363
10 " "	0.6	0.595	0.782	1.363
15 " "	0.6	0.595	0.782	1.363
20 " "	0.6	0.595	0.782	1.363

Impressed voltage was increased.

Time	Impressed E. M. F. Volts	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
½ min. later	1.0	+0.997	—0.477	—1.474
5 " "	1.0	0.984	0.505	1.502
10 " "	1.0	0.984	0.505	1.502
15 " "	1.0	0.987	0.505	1.502
20 " "	1.0	0.987	0.505	1.502

Impressed voltage was increased.

½ min. later	1.4	+1.386	—0.238	—1.620
5 " "	1.4	1.386	0.238	1.620
10 " "	1.4	1.386	0.238	1.620
15 " "	1.4	1.386	0.238	1.620
20 " "	1.4	1.386	0.238	1.620

Laboratory of Applied Electrochemistry,
University of Wisconsin.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

NEW CELL ARRANGEMENT FOR DIRECT DETERMINATION OF THE "FREE ENERGY."

By Reinhard Beutner.*

It is well known that the e. m. f. of a reversible galvanic cell is a most important datum in theoretical chemistry, being proportional to the free energy of the reaction which takes place in the cell. However, this electrometric measurement has only been possible for some reactions. Also, for most cell arrangements generally used, the relation between e. m. f. and the free energy value of the corresponding reaction (which can be calculated from Helmholtz's formula $A - U = T\frac{dA}{dT}$) is by no means a simple one. One reason is that most cells contain potential differences at the junction of miscible electrolytes (so-called diffusion potentials), which depend on ionic mobilities, according to very complicated relations. They therefore must be subtracted from the total e. m. f. observed in order to get a quantity related to the free energy.

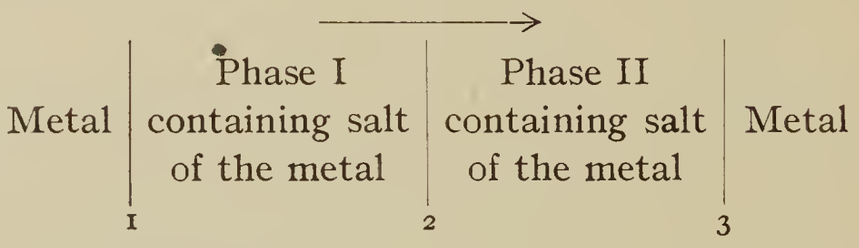
The cells described in this paper are built up from immiscible electrolytes only (mostly solid salts). They are arranged in such a manner that no changes in concentration can arise within one phase, and equilibrium exists at all junctions of two phases. No diffusion potentials can therefore exist. The problem to find the corresponding galvanic cell for any definite chemical reaction may be solved in many cases by means of these cell arrangements; the e. m. f. is always directly proportional to the free energy.

The characteristic property of such cell arrangements therefore would be that their e. m. f. is composed exclusively of potential differences at the junction of immiscible electrolytic conductors.

* A contribution from the Rockefeller Institute for Medical Research, New York. Translated from the German by J. W. Richards.

In two previous papers communicated to this Society the author has reported on investigations concerning such potential differences.

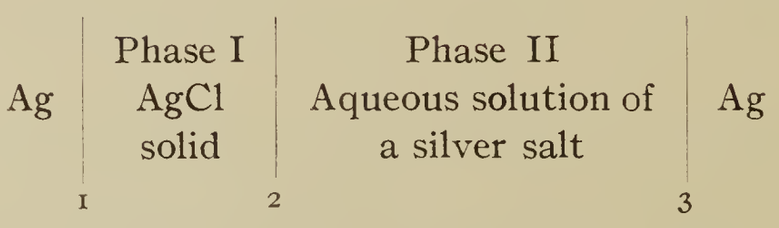
It was mentioned that they can be calculated from the ratio of the ionic concentrations in the two phases. A calculation of this kind is, however, not practical for the problem of this paper. In order to properly understand the electrochemical significance of phase junctions, cell arrangements of the general type



may again be considered here.[1] The two electrolytic phases are in equilibrium with each other as well as with the metal. In such a cell, therefore, no reaction can take place even with a current passing through the system. The only change which a current brings about is the transportation of metal from one electrode, *i. e.*, with a current passing in the direction of the arrow, metal will be apparently transformed into salt or ion in phase I, while at 3 the opposite change takes place, metal being formed from the electrolyte of phase II. It seems, therefore, as if phase I would be increased, phase II decreased; this, however, is impossible, as mentioned above. *It is to be concluded that the increase of phase I at junction 1 and the decrease of phase II at junction 3 is counterbalanced by a change taking place at 2, where an equivalent mass of the metallic ion passes from phase I into phase II.*

This general consideration may be elucidated by some more special cases.

The cell



[1] This theory is explained in a somewhat different way by Haber (Annalen der Physik [IV] 26 927), who also mentions some of the cell arrangements described below.

may serve as an example. Phase I is here represented by an uninterrupted layer of solid AgCl, phase II by an aqueous solution of a silver salt. As AgCl is insoluble in water, the two electrolytic phases are in equilibrium and the e. m. f. of cell is equal to zero. At the junction of AgCl and $Ag^{\bullet}$ solution, Ag ion will therefore pass from AgCl solid into the solution or in the opposite direction.

Another example is the cell

$$\mathrm{Ag} \;\Big|\; \begin{matrix}\mathrm{AgCl}\\ \text{solid}\end{matrix} \;\Big|\; \begin{matrix}\mathrm{Ag_2SO_4}\\ \text{solid}\end{matrix} \;\Big|\; \mathrm{Ag}$$

which has also the e. m. f. zero, since the solid salts AgCl and Ag_2SO_4 are immiscible. At the middle junction the transformation takes place

$$Ag^{\bullet} \text{ in } AgCl \longrightarrow Ag^{\bullet} \text{ in } Ag_2SO_4$$

The theoretical conclusions were controlled by experiment in this case and verified. With the phase junctions mentioned so far, one kation is common to both phases; apparently there must be one common ion in order to make the potential difference reversible, but also such potential differences are of course reversible which are located at the junctions of phases which have one negative ion common to both phases. Thus, at the junction of AgCl and NaCl the potential difference is defined by the transformation

$$\underset{\text{in AgCl}}{Cl'} \longrightarrow \underset{\text{in NaCl}}{Cl'}$$

which takes place if a current passes from AgCl to NaCl. This can be proved in the same way as for potential differences mentioned above. The cell

$$\underset{\text{electrode}}{Cl} \;\Big|\; AgCl \;\Big|\; NaCl \;\Big|\; \underset{\text{electrode}}{Cl}$$

must have zero e. m. f., as it is in a perfect state of equilibrium. With a current passing from left to right, Cl′ enters into AgCl and is deposited from NaCl; at the middle junction it therefore passes from AgCl into NaCl. An analogous cell for the junction Ag_2SO_4 and Na_2SO_4 could not be realized, since SO_4'' electrodes

do not exist; there is no doubt, however, that also at this junction a potential difference corresponding to the transformation

$$SO_4'' \text{ in } Ag_2SO_4 \longrightarrow SO_4 \text{ in } Na_2SO_4$$

exists.

Our fundamental problem, to find a galvanic cell for any chemical reaction, can be solved in many cases by finding a suitable combination of potential differences between metals and electrolytes or between two immiscible electrolytes. These last potential differences may be defined either by a common negative or a common positive ion.

The solution of our problem demands, however, in many cases the application of what I have named "intermediate salts" (Zwischensalze). *Such are all electrolytic phases which, inserted as a middle conducting layer in a galvanic cell, remain unchanged if a current passes, while they deposit the same ion on one side as enters into them at the other side.* Intermediate salts can be inserted either at *phase junctions of two solid salts* without affecting the e. m. f. (*e. g.,* between AgCl and NaCl, any chloride) or *at the junction of a metal and a salt* (*e. g.,* between Ag metal and AgCl solid, any Ag salt). Furthermore, they can be inserted between miscible phases, and it may be thus possible to measure potential differences between miscible phases as though they were immiscible. The main purpose of this paper is to illustrate the usefulness of this principle for electrometric determinations of the free energy.

In all the following deductions, however, the assumption is made that all *chemical elements,* metals and metalloids conduct the current without transportation of weighable mass and that all chemical compounds (salts) conduct as electrolytes.

This does not hold for certain oxides and sulphides (like CuO and Cu_2S), but it holds for most other salts, even in the solid state, as has been proved by experiments of Haber and Tolloçko, Lorenz and others. It has been proved also that solid salts are decomposed by electrolysis, and in some cases also the attempt has succeeded to apply to them Faraday's law. It may be very well assumed that Faraday's law holds good for all electrolytes in general, even if a quantitative proof has not been obtained.

We denote in the following general observations the metals

with *M, N* or *X;* positive elements *A. B. C.* In some instances, also, special cases may be described.

FORMATION OF SALTS FROM METAL AND METALLOID.

I. The simple reaction:

$$A + M = MA$$

is measured by the element

$$A \mid MA \mid M \qquad \text{(Ia)}$$

These kinds of cells with solid[2] or melted salts have been investigated by Lorenz and his co-workers. Applying the "intermediate salt rule" to this case, it says that the arrangement

$$\begin{array}{c|c|c|c|c} M & \begin{array}{c}MC\\ \text{solid}\end{array} & \begin{array}{c}MA\\ \text{solid}\end{array} & \begin{array}{c}ZA\\ \text{solid}\end{array} & A^{3} \\ & 1 & 2 & 3 & 4 \end{array} \qquad \text{(Ib)}$$

has the same current-generating variations and e. m. f. MC and ZA must then be so chosen that equilibrium prevails at all contacts of phases in the cell; that is, the salts in contact must not form mixed crystals, and the temperature must remain under the cryohydric points of the two salts in contact. MC then remains unchanged, since when current flows in the direction of the arrow there arises at the phase-limit 1 new $M^{\bullet}$-ions; at 2 a like number pass over into MA, while ZA remains unchanged, since it gives over to MA the A'-ions received by the electrode. MA experiences on one side an increase of A ions, on the other side an increase of M ions; the operation is similar to that in (Ia). One arrives at the same result by the following more exact proof: One assumes inserted in the center of the cell (Ib), in the solid MA, an M electrode and an A electrode, as follows:

$$M \mid MC \mid MA \mid \underbrace{M \mid MA \mid A}_{\text{inserted}} \mid MA \mid ZA \mid A$$

[2] Lorenz and Czepinski: Zeitschr. f. anorg. Chem., **19**, 208 (1899); Lorenz and O. H. Weber: Ibid. **21**, 305 (1899); Katayama: Zeitschr. f. physik. Chem., **61**, 566 (1907); Lorenz and Katayama: Ibid., **62**, 119 (1908).

[3] Limits of phases will be indicated by vertical lines; changes of concentration within a phase by points.

The cell is thereby subdivided into the partial cells:

$$M \mid MC \mid MA \mid M \qquad M \mid MA \mid A \qquad A \mid MA \mid ZA \mid A$$

The two outer cells have zero e. m. f., according to the above developed principles; the center one is identical with (Ia).

II. The application of the intermediate-salt rule is of particular importance when it is a question of measuring reactions in which the resulting salts form two stages of oxidation or valence, *e. g.*, the reaction $2Cu + Cl_2 = 2CuCl$. Such an element as

$$\begin{array}{c|c|c} Cu & \begin{matrix} CuCl \\ solid \end{matrix} & Cl_2 \end{array}$$

cannot be stable, for the Cl_2 forms $CuCl_2$ by local action, and the cell transforms itself into the following:

$$\begin{array}{c|c|c|c} Cu & \begin{matrix} CuCl \\ solid \end{matrix} & \begin{matrix} CuCl_2 \\ solid \end{matrix} & Cl_2 \\ & \longrightarrow & & \end{array} \qquad \text{(Ic)}$$

In this cell a further change is impossible if CuCl and $CuCl_2$ are immiscible and the $CuCl_2$ surrounds the Cl_2 electrode as a compact mass.

Assuming the electromotive behavior of the phase borders and the intermediate-salt rule as unknown, it appears doubtful what is the current-generating reaction in this cell, since when current flows in the direction of the arrow CuCl is formed at the Cu electrode and $CuCl_2$ at the Cl_2 electrode. As a matter of fact, only CuCl can be formed in the cell, since $CuCl_2$ behaves as an intermediate-salt between the Cl_2 electrode and the CuCl. Against this it might be objected that CuCl might also be considered as an intermediate salt between Cu and $CuCl_2$, but two independent proofs can be given that the result stated is correct, each leading to interesting further conclusions.

1. *Proof:* Assuming that there exists a cuprous salt CuX which spontaneously decomposes into Cu and the corresponding cupric salt CuX_2, according to the reaction:

$$\underset{\text{solid}}{2CuX} = Cu + \underset{\text{solid}}{CuX_2}$$

This cupric salt, which therefore must be stable in presence of Cu, can be assumed connected up in the center of phase II of the cell (Ic), with another Cu electrode within it, thus:

$$Cu \mid CuCl \mid CuCl_2 \mid \underbrace{CuX_2 \mid Cu \mid CuX_2}_{\text{connected in}} \mid CuCl_2 \mid Cl_2$$

The cell is thereby resolved into the constituent cells:

$$\begin{array}{ccccccccc} Cu & | & CuCl & | & CuCl_2 & | & CuX_2 & | & Cu \\ & & I & & II & & III & & \\ & & 1 & & 2 & & 3 & & 4 \end{array} \qquad \text{(Id)}$$

and:

$$\begin{array}{ccccccc} Cu & | & CuX_2 & | & CuCl_2 & | & Cl^2 \\ & & I & & II & & \\ & & 1 & & 2 & & 3 \end{array} \qquad \text{(Ie)}$$

In (Id) 2Cu metal goes over into 2CuCl for each 2 Faradays passing the phase limit 1 in the direction of the arrow; the necessary Cl ions pass inward through the phase limit 2. At the phase limit 3, for the same 2 F. of current, one bi-valent Cu ion passes over into CuX_2, while a similar amount of Cu metal is separated out of it; CuX_2 is therefore an intermediate salt. Since more Cu goes into the salt on the left than is separated out of the salt on the right, because of the difference in valence of CuCl and CuX_2, the whole change corresponds to the reaction:

$$Cu + CuCl_2 = 2CuCl.$$

(By such means, likewise on the basis of the intermediate-salt rule, it is possible to investigate certain oxidation and reduction reactions which can otherwise only be measured with unattackable electrodes.)

CuX_2 acts as an intermediate salt in the cell (Ie), for the same reasons as in cell (Id); the main reaction is therefore:

$$Cu + Cl_2 = CuCl_2.$$

The sum of these two reactions corresponds to the reaction of the cell (Ic); and one has:

$$Cu + CuCl_2 + Cu + Cl_2 = CuCl_2 + 2CuCl,$$

or:

$$2Cu + Cl_2 = 2CuCl,$$

as was asserted.

2. *Proof:* One imagines the chloride of another metal, unaffected by chlorine, such as AgCl, connected in the middle of phase I of the cell (Ic), and also a Cl_2 electrode therein; that is:

$$Cu \mid CuCl \mid \underbrace{AgCl \mid Cl_2 \mid AgCl}_{\text{connected in}} \mid CuCl \mid CuCl_2 \mid Cl_2$$

The cell may be resolved into the constituent cells:

$$Cu \mid CuCl \mid AgCl \mid Cl_2 \qquad \text{(If)}$$

and

$$Cl_2 \mid AgCl \mid CuCl \mid CuCl_2 \mid Cl_2. \qquad \text{(Ig)}$$

In the cell (If) AgCl is an intermediate salt, and the reaction is therefore:

$$2Cu + Cl_2 = 2CuCl.$$

The e. m. f. of the last constituent cell is, however, zero, since none of the chlorides in it can be altered by the passage of the current.

III. In all the cells mentioned, each solid salt can be replaced by its saturated solution, or in general by any phase which stands in equilibrium with it, provided that the neighboring phases likewise stand in equilibrium with the solution phase in question, and that complications by local action are avoided. In such cases the current-producing reaction and the e. m. f. of the cell are not changed. Intermediate salts can also be replaced by any desired solid or fluid *not* saturated solutions. So, for example, the cells:

$$A \mid \begin{matrix} MA \\ \text{solid} \end{matrix} \mid M$$

and

$$A \mid \begin{matrix} MA \\ \text{saturated solution} \end{matrix} \mid M$$

have equal e. m. f. Bodländer's[4] calculations of solubilities are known to rest on this fact. Likewise the cells:

Pb	$PbCl_2$ solid	$CuCl_2$ solid intermediate salt	Cl_2,

and

Pb	$PbCl_2$ solid	$CuCl_2$ unsaturated solution	Cl_2

have equal e. m. f. The $CuCl_2$ solution suffers no change in concentration by passage of the current. On the contrary, if the salt entering into reaction is used in an unsaturated solution, the e. m. f. is greater than with saturated solutions, since work is then gained from the osmotic forces in addition to the energy of formation of the salt. The e. m. f. rises with the dilution, and, in fact, it is shown by using the Nernst formula that the e. m. f. is proportional to the logarithm of the product of the ion concentrations when the dissolved salt is practically completely dissociated, or to the logarithm of the simple concentrations when the dissociation is extremely small.

FORMATION OF DOUBLE SALTS AND SALT HYDRATES.

I. It has heretofore not been attempted to measure the energy of formation of double salts; and without using intermediate salts such measurements are possible in only a very few cases. Such a reaction as, for example:

$$\underset{\text{solid}}{MA} + \underset{\text{solid}}{NA} = \underset{\text{solid}}{MNA_2}$$

passes into the cell:

M	MNA_2 + NA solid mixture	ZA' solid	MA solid	M
	1	2	3	4

(IIa)

$\longrightarrow$

As current passes in this cell in the direction of the arrow, MA is re-formed at the phase limits 1 and 2, since anions A' pass over out of ZA, and $M^{\bullet}$ ions form from the electrode. This MA is produced, however, not as the free salt MA, because

[4] Zeitschrift f. physik. Chem., 27, 55 (1898).

NA is present as a depolarizer, but as the compound MNA_2, using up for this purpose NA in equivalent quantity. It is clear that MA is used up on the other side of the cell. ZA remains unaltered, as an intermediate salt, because it has an ion in common with both of its neighboring phases; the conditions of equilibrium at the phase limits 2 and 3 must naturally be met, it is clear. The current-producing reaction therefore corresponds to the formation of the double salt. It is hereby assumed that MNA_2 and NA are present at the two-phase limits in sufficiently fine divisions so that the depolarizing action in question can occur. Reciprocal solubility of MNA_2 and NA may exist only to an extremely small degree. If this were not the case, the course of the reaction would evidently be associated with osmotic energy changes, and the reaction could no longer be regarded as simply a "fixed" reaction.

The cell (IIa) can also be built up in variously different ways. Such electrodes as M, N or A are in no way absolutely indispensable for the arrangement; any desired metal X can be used as electrode material. One could, for instance, connect up:

X	XA	MA	MC	MNA_2 + NA	XA	X
	I	II	III	IV	V	
	solid	solid	solid	solid mixture	solid	
	1 2		3 4		5 6	

$\longrightarrow$ (IIb)

If the same requirements are put upon this cell as upon (IIa), it will be found that the same reactions take place here when current passes. Still other similar schemes of connections could be given; we will merely note that in place of the intermediate salt ZA of the cell (IIa) a halogen electrode can be used when it is a question of forming a double salt from two halogen salts. One has in that case:

M	MNA_2 + NA	A	MA	M
	solid mixture	electrode	solid	

(IIc)

In general it can be said that any arrangement is suited to such measurements in which the solid mixture MNA_2 + NA on the one hand, and the solid salt MA on the other hand, are surrounded on the one side by a phase reversible in relation to M and on the other side by a phase reversible in respect to A, while the other potentials of the cell reciprocally compensate themselves.

It is also not absolutely necessary that pure solid salts be always used as intermediate salts; any solid or liquid solution which stands in equilibrium with the salts to be kept separated from each other can serve as an intermediate salt.

Further, such an element as the following can be used for measuring this reaction:

M	Saturated sol. of MNA_2 and NA (I)	ZA solid (II)	Saturated sol. of MA (III)	M
1		2	3	4

(IId)

The solvents used for the phases I and III need not be identical. When current passes in this cell in the direction of the arrow, MA is formed in phase I, and since NA is here present, MNA_2 is formed as solid salt because the saturation concentration is exceeded. Solid NA is consumed in this operation in equivalent quantity. The total change corresponds therefore to the reaction mentioned. In this it is assumed that MA, NA and MNA_2 form no hydrates with the solvent (water).

II. The formation of salt hydrates can be regarded as a particular case of formation of a complex salt. Example:

$$CuCl_2 + 2H_2O = CuCl_2.2H_2O,$$

which can be measured by help of the combination:

Cu	$CuCu_2.2H_2O$. Saturated aqueous sol. (I)	AgCl solid (II)	$CuCl_2$ Anhydrous, solid (III)	Cu
	1	2	3	4

(IIf)

In this cell, when current passes in the direction of the arrow, there is found in phase I solid hydrated cupric chloride, since $Cu^{\cdot\cdot}$ ions pass into it from the electrode and Cl' ions from the solid AgCl; the necessary water is taken out of the solution. Anhydrous $CuCl_2$ is similarly used up in phase III. The total change does *not,* however, correspond to the reaction $CuCl_2 + 2H_2O = CuCl_2.2H_2O$ in such a manner that the e. m. f. can be calculated from the thermochemical heat, as in "fixed" reactions. All those reactions can evidently be treated as "fixed" whose entire constituents form separate phases; that is, none of the materials which enter into the reaction equation can be contained in solu-

tion in another phase. This condition is not met in the cell (IIf), since $CuCl_2.2H_2O$ is soluble in H_2O to a considerable extent. If one imagines, however, 5 molecules of H_2O vapor distilled over isothermally and reversibly from pure water at vapor pressure P into the saturated aqueous solution of $CuCl_2$ at vapor pressure p, the work done is equal to $5RT.\ln\frac{P}{p}$ obtained (work negative). When current passes in the cell (IIf), mol. of $CuCl_2.2H_2O$ is produced from anhydrous salt and "diluted" water of the saturated solution, furnishing the work 2EF. The total yield of these two energy-furnishing processes corresponds to the equation:

$$\underset{\text{solid}}{CuCl_2} + \underset{\text{pure liquid}}{2H_2O} = \underset{\text{solid}}{CuCl_2.2H_2O}.$$

The motive force of this reaction can, however, be calculated from the heat evolution as for a "fixed" reaction; the circumstance that the water is present in the liquid form has no appreciable influence on the application of the Thomson rule, since it is so far removed from its critical point. Designating the e. m. f. calculated from the heat evolution as E_w, and the measured e. m. f. by E_g, we have:

$$2E_w.F = 2E_g.F + 5RT \ln\frac{P}{p},$$

$$E_g = E_w - \frac{5}{2}\frac{RT}{F}\ln\frac{P}{p}$$

The quantities P and p can be measured; accurate vapor tension determinations have been already made for some saturated solutions.[5]

SUBSTITUTION OF A COMBINED METAL.

I. Reactions of the type:

$$\underset{\text{solid}}{MA} + N = \underset{\text{solid}}{NA} + M$$

occur in such cells as:

$$\underset{1}{M} \;\big|\; \underset{\text{solid}}{MA} \;\big|\; \underset{2}{\underset{\text{solid}}{NA}} \;\big|\; \underset{3}{N} \qquad \text{(IIIa)}$$

[5] See, for example, A. Speranski: Zeitschr. f. physik. Chem., 70, 519 (1910).

Such cells have been investigated by Lorenz and Katayama.[6] If the formation of mixed crystals between MA and NA is excluded, the driving force of the reaction can be measured with this cell beneath the cryohydric point of MA and NA. Above that point, or if the formation of mixed crystals between MA and NA is not excluded, the e. m. f. can be measured as though MA and NA were not miscible by inserting in the circuit an intermediate salt at 2. Intermediate salts may also be inserted at 1 and 3 without influencing the e. m. f. The general form of the cell is therefore:

M	MC solid	MA solid	ZA solid	NA solid	NC′ solid	N	(IIIb)

Katayama's measurements proved that the e. m. f. of such a cell as (IIIa) with solid salts corresponds to the free energy of the substitution reaction. It was found, for instance, that the difference of the e. m. f.s of the single arrangements:

Ag	AgCl solid	Cl_2 and Pb	$PbCl_2$ solid	Cl_2

were equal to that of the cell:

Ag	AgCl solid	$PbCl_2$ solid	Pb	(IIIc)

within the errors of measurement. The single arrangements undoubtedly correspond to:

$$2Ag + Cl_2 = 2AgCl, \text{ and } Pb + Cl_2 = PbCl_2,$$

but the differences between these give the reaction equation:

$$Pb + 2AgCl = PbCl_2 + 2Ag.$$

The following table shows the agreement:

Temp. C°	Ag | AgCl | Cl_2 Volt	Pb | $PbCl_2$ | Cl_2 Volt	Difference Volt	Ag | AgCl | $PbCl_2$ | Pb Volt	Δ Volt
60°	1.106	1.581	0.475	0.480	+0.005
70	1.100	1.575	0.475	0.479	+0.004
80	1.094	1.568	0.474	0.478	+0.004
90	1.088	1.562	0.474	0.477	+0.003
100	1.082	1.555	0.473	0.476	+0.003
110	1.076	1.549	0.473	0.475	+0.002
120	1.070	1.542	0.472	0.474	+0.002
130	1.064	1.536	0.472	0.473	+0.001
140	1.058	1.529	0.471	0.472	+0.001

[6] Katayama: Zeitschr. f. physik. Chem., **61**, 566; Lorenz and Katayama: Ibid., **62**, 119 (1908).

The deviation is greater at lower temperatures, due most probably to the increased difficulty of the measurement in consequence of increase of the internal resistance.

Lorenz and Weber[7] have also investigated cells of the type of the Daniell battery, using molten electrolytes; for instance:

$$\underset{\text{melted}}{\text{Ag} \mid \text{AgCl}.....\text{PbCl}_2} \mid \text{Pb} \qquad \text{(IIId)}$$

In contradistinction to (IIIc), the e. m. f. of this cell does not correspond to the free energy of the reaction of substitution, since AgCl and $PbCl_2$ are miscible, like almost all melted salts. There is therefore no phase limit between them at which a resulting chemical equilibrium of transfer of $Cl_{\text{in AgCl}} \longrightarrow Cl_{\text{in PbCl}_2}$ can take place, but there is rather a transfer through mixed layers. As Lorenz and Weber themselves remarked, the real differences in this case between $Ag \mid AgCl \mid Cl_2$ and $Pb \mid PbCl_2 \mid Cl_2$ are not equal to that of cell (IIId); "the deviations are all positive and greater than the errors of the investigation." The following table, taken from the work mentioned, shows this:

Temperature C°	Difference of the Cells $Ag \mid AgCl \mid Cl_2$ and $Pb \mid PbCl_2 \mid Cl_2$	$Ag \mid AgCl.....PbCl_2 \mid Pb$ Melted	Δ
520°	0.379	0.349	0.030
530	0.375	0.345	0.031
540	0.372	0.341	0.031
550	0.369	0.338	0.031
560	0.366	0.334	0.032
570	0.363	0.330	0.033
580	0.360	0.327	0.033
590	0.357	0.323	0.034
600	0.355	0.320	0.035
610	0.352	0.316	0.036
620	0.350	0.312	0.038
630	0.349	0.309	0.040
640	0.348	0.305	0.043
650	0.346	0.302	0.044
660	0.345	0.298	0.047
670	0.344	0.294	0.050

II. It must be expressly stated that it is not possible to use a cell of the type of a Daniell battery, such as

$$Cu \mid CuSO_4 \text{ solution} \quad — \quad ZnSO_4 \text{ solution} \mid Zn$$

[7]Lorenz and Weber: Zeitschr. f. anorg. Chem., **21**, 305; see also Lorenz and Suchy: Ibid., **19**, 283.

for measuring the e. m. f. of the reaction:

$$\underset{\text{solid}}{CuSO_4} + Zn = \underset{\text{solid}}{ZnSO_4} + Cu$$

as Halla has already pointed out.[8] The reason is that between the copper sulphate solution and the zinc sulphate solution there is no phase limit, since the two solutions are miscible.

It is, however, possible to devise arrangements utilizing the intermediate-salt rule, which contain homogeneous phases and which can be used for direct measurement of the free energy of the reaction. Such an arrangement is obtained, for instance, if a sulphate insoluble in water is connected in circuit between the $CuSO_4$ and $ZnSO_4$ solutions. Another method is to make a solution saturated with both $CuSO_4$ and $ZnSO_4$ and to put solid $ZnSO_4$ between this and the Zn electrode, as follows:

$$Cu \mid \underset{\text{saturated solution}}{CuSO_4 + ZnSO_4} \mid \underset{\text{solid}}{ZnSO_4} \mid Zn$$

This field has not been worked over experimentally, but it may be mentioned in this connection that, as Negbaur[9] has shown, the cells

$$Ag \mid \underset{\text{solid}}{AgBr} \mid \underset{\text{solid}}{PbBr_2} \mid Pb$$

and

$$Ag \mid \underset{\text{solid}}{AgBr} \mid \underset{\text{saturated solution}}{PbBr_2} \mid Pb$$

have the same e. m. f. This proves, therefore, that, as was to be expected, a solid salt in a cell can be replaced by its saturated solution if by so doing no diffusion potentials are introduced.

DOUBLE DECOMPOSITIONS.

The examples so far described were of a comparatively simple nature, and were intended to illustrate the principal difference between the cell arrangements heretofore used in electrochemistry and the new ones proposed in this paper. The experimental proofs of these new cells are, unfortunately, lacking in many

[8] Zeitschr. f. Elektrochem.

[9] Annal. d. Physik., (3) **47**, 27 (1892).

cases. In the examples now to be cited, an experimental testing has been carried out, and has proved in a highly striking manner the fruitfulness of the above-explained methods.

I. Double decompositions between solid immiscible salts:

$$\underset{\text{solid}}{MA} + \underset{\text{solid}}{NB} = \underset{\text{solid}}{MB} + \underset{\text{solid}}{NA}$$

can be investigated electrochemically in cells of the construction:

$$\underset{\longrightarrow}{M \mid \underset{\text{solid}}{MA} \mid \underset{\text{solid}}{NA} \mid \underset{\text{solid}}{NB} \mid \underset{\text{solid}}{MB} \mid M} \qquad \text{(IVa)}$$

On flow of current in the direction of the arrow, MA increases, MB must decrease, while the A′ ions necessary for the increase of MA must come out of NA, which therefore also decreases. The B′ ions given up by MB go over into NB, which likewise increases. This amounts to just the total change corresponding to the double decomposition.

Every electrode which is reversible in relation to the ions M, N, A or B can be used for constructing this cell. The arrangements:

$$N \mid NA \mid MA \mid MB \mid NB \mid N, \qquad \text{(IVb)}$$

$$A \mid NA \mid NB \mid MB \mid MA \mid A, \qquad \text{(IVc)}$$

$$B \mid NB \mid NA \mid MA \mid MB \mid B, \qquad \text{(IVd)}$$

have therefore the same e. m. f. as the cell (IVa); likewise the e. m. f. of this cell is not changed by the insertion of intermediate salts at any desired phase limit. The extraordinary versatility of the arrangements possible for investigating similar double decompositions is still further increased by the fact that any desired metal X can be used as electrode material. For instance:

$$X \mid \underset{\text{I}}{XA} \mid \underset{\text{II}}{NA} \mid \underset{\text{III}}{NB} \mid \underset{\text{IV}}{MB} \mid \underset{\text{V}}{MA} \mid \underset{\text{VI}}{XA} \mid X \qquad \text{(IVe)}$$

The changes in the phases I and IV in this cell compensate each other, as in cell (IIb). Further, the solid salts can, under suitable conditions, be replaced by saturated solutions.

EXPERIMENTAL CONFIRMATIONS OF THE THEORY.

We will now speak of the experimental confirmations of the theory, taken from the author's dissertation for the Doctorate (carried out in Professor Haber's laboratory in 1908). The leading idea in these tests was to establish the localization of the e. m. f. at the phase limits in these cells.

II. The first example measured was the reaction:

$$Ag_2SO_4 + 2NaCl = Na_2SO_4 + 2AgCl$$

the corresponding cell being:

$$+ \text{ Ag} \mid Ag_2SO_4 \mid Na_2SO_4 \mid \text{NaCl} \mid \text{AgCl} \mid \text{Ag} - \qquad \text{(IVf)}$$

The calculated e. m. f. from the thermochemical measurements of Thomson was 0.535 volt, from Berthelot's heat values 0.515 volt.

observed { at $t = 160°$ 0.530 to 0.535 volt during 30 minutes.
$t = 310°$ 0.530 to 0.534 volt during 60 minutes.

These tests show that the e. m. f. is independent of the temperature, and justify placing V = A, in agreement with the Helmholtz formula. In other words, the e. m. f. follows from the thermochemical heat by dividing it by 2 × 96,540. Thomson gives 24,960 calories = 103,350 Joules, which divided by 2 × 96,540 = 0.535 volt. In regard to making such measurements, the solid nearly anhydrous salts were pressed upon each other as pastilles in a steel mould, so as to produce plainly separated layers; the pastilles were about 1 cm. in diameter by 2 cm. high; these salts were then placed between two small silver plates. The e. m. f. must be measured at 150° or over, else a measurement is impossible, even with an electrometer, because of the extremely small conductivity. The upper temperature limit was the softening point of the salt mass, forming eutectic mixtures, in this case, about 350° C. It was also found necessary to melt the AgCl before using it in a current of dry Cl_2. A series of tests where this was omitted gave values varying about 6 percent, and the AgCl became deep black during the heating,[10] from formation of metal or sub-chloride; this decomposition must naturally have affected the measured e. m. f.

[10] These disagreeing values are given in Zeitschr. f. Elektrochem. **15**, 433 (1909).

The intermediate-salt rule was established with this cell by the following measurements: The cell (IVf) was taken, and AgCl connected in between Ag and Ag_2SO_4, thus:

$$+ \text{ Ag} \mid \overbrace{\text{AgCl} \mid \text{Ag}_2\text{SO}_4}^{\text{intermediate salt}} \mid \text{Na}_2\text{SO}_4 \mid \text{NaCl} \mid \text{AgCl} \mid \text{Ag} - \quad \text{(IVg)}$$

measured at $\begin{cases} t = 250^\circ \ldots 0.522 \text{ to } 0.523 \text{ volt during 20 minutes.} \\ t = 310^\circ \ldots 0.525 \text{ to } 0.534 \text{ volt during 150 minutes.} \end{cases}$

This is in fine agreement with the values of the cell (IVf). In this cell the electrodes are completely symmetrical, and the potential differences arise only between electrolytic conductors.

Another example was made by inserting in cell (IVf) LiCl between AgCl and NaCl, and Li_2SO_4 between Ag_2SO_4 and Na_2SO_4, giving the cell:

$$- \text{ Ag} \mid \text{AgCl} \mid \text{LiCl} \mid \text{NaCl} \mid \text{Na}_2\text{SO}_4 \mid \text{Li}_2\text{SO}_4 \mid \text{Ag}_2\text{SO}_4 \mid \text{Ag} + \quad \text{(IVh)}$$

This gave, at $t = 210^\circ$ 0.513 to 0.532 volt, during 60 minutes. The variations were considerable because the temperature was comparatively low.

$t = 247^\circ$ 0.529 to 0.537 volt during 60 minutes.
$t = 271^\circ$ 0.520 to 0.532 volt during 45 minutes.

A cell of the type (IVe), without Ag electrodes, was constructed to test the reaction:

$$\text{Ag}_2\text{SO}_4 + \text{NaCl} = \text{AgCl} + \text{Na}_2\text{SO}_4$$

The cell was arranged as follows:

$$- \text{ Pb} \mid \text{PbCl}_2 \mid \text{NaCl} \mid \text{Na}_2\text{SO}_4 \mid \text{Ag}_2\text{SO}_4 \mid \text{AgCl} \mid \text{PbCl}_2 \mid \text{Pb} + \quad \text{(IVi)}$$

$t = 210^\circ$ 0.489 to 0.494 volt
$t = 262^\circ$ 0.488 to 0.498 volt
$t = 310^\circ$ 0.493 to 0.497 volt

The variations amount here to almost 10 percent, and the reason for them is not fully cleared up; possibly the oxidation of the base Pb electrodes is the cause. However, these experiments

show that it is possible to measure a reaction between Ag salts and Na salts, using Pb electrodes or electrodes of any other desired metal.

This also makes it possible to measure reactions between salts of quite base metals, using electrodes of noble metals. Take, for instance, the reaction:

$$BaCl_2 + 2KF = BaF_2 + 2KCl.$$

It would be only with the greatest difficulty that electrodes of metallic Ba or K could be used experimentally, but, thanks to the intermediate-salt rule, it is easily possible to find an arrangement using Ag electrodes which permits of measuring the desired reaction; for instance:

$$+ \text{ Ag} \mid \text{AgCl} \mid \text{KCl} \mid \text{KF} \mid \text{BaF} \mid \text{BaCl}_2 \mid \text{AgCl} \mid \text{Ag} - \quad \text{(IVk)}$$

measured { 0.308 to 0.312 volt at 305°
0.305 to 0.308 volt at 210°

Calculated from the thermochemical data, one obtains 0.340 volt, taking the values of Petersen and Guntz, 0.151 volt taking Berthelot's measurements. The values found lie considerably nearer to Petersen and Guntz's measurements. It is thus possible to check up independently the often erroneous heat data by measurements of the e. m. f. of properly devised cells. By an entirely similar arrangement the reaction between $SrCl_2$ and KF was measured, for which Petersen and Guntz's thermochemical data gave 0.585 volt, Berthelot's 0.352 volt. Measurement gave in this case an average value of 0.437 volt.

III. On account of the importance of the intermediate-salt rule in the setting up of cells, we will give here that proof of its validity which shows most strikingly the characteristic applications of the rule.

The following arrangement was measured:

$$- \text{ Pb} \mid \text{PbCl}_2 \mid \text{SrCl}_2 \mid \text{SrF}_2 \mid \text{PbF}_2 \mid \text{Pb} + \quad \text{(IVl)}$$

$$\longrightarrow$$

Reaction: $PbF_2 + SrCl_2 = PbCl_2 + SrF_2$

Calculated: { 0.315 volt (Petersen and Guntz)
0.377 volt (Berthelot)

Observed: 0.302 volt (mean value between 210° and 260°).

KCl was then inserted between $PbCl_2$ and $SrCl_2$, and KF between SrF_2 and PbF_2. The following cell was then measured:

$$- \text{ Pb} \mid PbCl_2 \mid \text{KCl} \mid SrCl_2 \mid SrF_2 \mid \text{KF} \mid PbF_2 \mid \text{Pb} + \qquad \text{(IVm)}$$

The e. m. f. now measured was an average of 0.255 volt, deviating considerably from the above 0.30 volt. Considering the large experimental difficulties, this deviation may probably be ascribed to experimental errors. Measurements with Pb electrodes and Pb salts are always accompanied by greater uncertainties than those with Ag salts and Ag electrodes.

If the two Sr salts are left out of the above arrangement, giving:

$$+ \text{ Pb} \mid PbCl_2 \mid \text{KCl} \mid \text{KF} \mid PbF_2 \mid \text{Pb} - \qquad \text{(IVn)}$$

the polarity of the cell is reversed. This is to be expected, because the determining reaction in this arrangement is not the reaction of PbF_2 and KCl, but rather the reverse: $PbCl_2 + 2KF \longrightarrow PbF_2 + 2KCl$. This reversal of the poles was actually observed. The amount of observed e. m. f. was 0.231 volt (mean value at 310°), while calculation from Petersen and Guntz's thermochemical values give 0.21 volt, from Berthelot's 0.024 volt.

If in the cell (IVm) the K and Sr salts are exchanged, so that the Sr salts become the intermediate salts, the same result is obtained. The cell:

$$+ \text{ Pb} \mid PbCl_2 \mid SrCl_2 \mid \text{KCl} \mid \text{KF} \mid SrF_2 \mid PbF_2 \mid \text{Pb} - \qquad \text{(IVo)}$$

has the same e. m. f. as (IVn), as was to be expected from the theory, because in this case the determining reaction is:

$$PbCl_2 + 2KF \longrightarrow PbF_2 + 2KCl$$

Measurement gave about the same value of e. m. f., *viz.*, 0.223 volt at 279°.

The cells (IVo) and (IVm) contain the same salts, only in a different order:

$$- \text{ Pb} \mid PbCl_2 \mid \text{KCl} \mid SrCl_2 \mid SrF_2 \mid \text{KF} \mid PbF_2 \mid \text{Pb} +$$
$$+ \text{ Pb} \mid PbCl_2 \mid SrCl_2 \mid \text{KCl} \mid \text{KF} \mid SrF_2 \mid PbF_2 \mid \text{Pb} -$$

Measured: 0.25 and 0.22 volt, respectively.

The reversal of the poles simply by reversing the middle pair of salts is a phenomenon which has never been observed in any

previous cell arrangement; this proves also the further fact that the laws which govern the e. m. f. of such arrangements are considerably different from those previously known.

IV. Cells like the preceding, but with saturated solutions in place of the solid salts, are not yet known or investigated. As was explained above in using the example of the Daniell cell, it is, however, not practicable to substitute saturated solutions for solid salts if diffusion potentials thereby arise. Also, a solid salt can naturally not be replaced by a solution saturated by its hydrate.

Let us see, for instance, in what manner, in a cell such as (IVf):

— Ag	AgCl solid	KCl solid	K_2SO_4 solid	Ag_2SO_4 solid	Ag +		(IVp)

the solid salts can be replaced by saturated solutions. Evidently it is not possible to replace the K_2SO_4 by its saturated solution, because a local reaction between KCl and Ag_2SO_4 will thereby be brought about; however, KCl and Ag_2SO_4 could indeed be replaced by their respective saturated solutions. It is one of the conditions of the equilibrium that these solutions be also saturated with respect to the neighboring salts; one would have then the following arrangement:

Ag	AgCl	Saturated solution of AgCl, KCl and K_2SO_4	K_2SO_4	Saturated solution of Ag_2SO_4 and K_2SO_4	Ag	(IVq)

The solid AgCl can also be left out of this combination, since it acts as an intermediate salt between Ag metal and the saturated AgCl solution. In this form:

Ag	Ag_2SO_4 + K_2SO_4 saturated solution I	K_2SO_4 solid II		K_2SO_4 + KCl + AgCl saturated solution III	Ag	(IVr)
	1	2	→	3	4	

the cell contains still only one single solid salt lying in the path of the current. The inner resistance can thereby be brought down to a much lower value than in cells with solid salts, and

this greatly facilitates the measurement of the e. m. f., which in these solution cells must exactly correspond to the free reaction energy.

In order to be sure that such a cell really fulfils the same purpose as if it were built up only of solid salts, let us discuss the mechanism of the development of current in the last named cell. When current passes in the direction of the arrow, $Ag^{\bullet}$ ions pass into phase I through the phase limit 1, solid Ag_2SO_4 separates out, SO_4'' ions are hereby withdrawn from the solution, but returned as solid K_2SO_4 goes into solution. The excess of $K^{\bullet}$ thus caused is carried over by the current through phase limit 2 into the solid K_2SO_4. At the phase limit 4, Ag is used up, solid AgCl goes into solution, the excess of Cl' precipitates out KCl and the $K^{\bullet}$ necessary for this comes out of solid K_2SO_4. Therefore the same double decomposition takes place as in cell (IVp). As for the mechanism of current generation, other explanations could be devised, as, for instance, by assuming SO_4'' as carrier of electricity through phase II; but all these elaborated mechanisms are of equal importance, as follows from thermodynamical principles. Phase II could, moreover, be replaced by a SO_4'' electrode of the second class.

V. There remains yet a second possible method of building up a similar cell with saturated solutions with only one solid salt in the path of the current. This method is particularly worth notice because of its relation to the cells with aqueous electrolytes such as those investigated by Bredig and Knüpffer. We imagine in cell (IVp) a salt difficultly soluble in water, such as $CaSO_4$, inserted between K_2SO_4 and Ag_2SO_4, as follows:

— Ag	AgCl solid	KCl solid	K_2SO_4 solid	$CaSO_4$ intermediate salt solid	Ag_2SO_4 solid	Ag +	(IVs)

This does not change the e. m. f. In this arrangement, AgCl, KCl and K_2SO_4 can be replaced by a combined saturated solution, and Ag_2SO_4 likewise by a saturated solution, giving:

— Ag	Solution saturated with AgCl, KCl, K_2SO_4 and $CaSO_4$	$CaSO_4$ solid	Solution saturated with Ag_2SO_4 and $CaSO_4$	Ag +	(IVt)

This cell has the particular characteristic, compared with cell (IVa), that the solutions containing KCl and K_2SO_4 can be used even not saturated with these salts. We therefore use the KCl and K_2SO_4 in aqueous solution at such dilution that they are practically completely dissociated. We then have:

Ag	Solution of SO_4'' and Cl' saturated with AgCl and $CaSO_4$	$CaSO_4$	Saturated solution of Ag_2SO_4	Ag	(IVu)

The determining reaction in this arrangement is now no longer the reaction:

$$\underset{\text{solid}}{AgSO_4} + \underset{\text{solid}}{2KCl} = \underset{\text{solid}}{K_2SO_4} + \underset{\text{solid}}{2AgCl}$$

but:

$$\underset{\text{solid}}{Ag_2SO_4} + \underset{\text{dissolved}}{2Cl'} = \underset{\text{solid}}{2AgCl} + \underset{\text{dissolved}}{SO_4''}$$

and, according to van't Hoff's principle of reaction isotherms, the free energy as also the e. m. f. depends on the concentration of the Cl' and SO_4''.

The type of these reactions is the same as the following:

$$\underset{\text{solid}}{TlSCN} + Cl = \underset{\text{solid}}{TlCl} + SCN$$

which reaction was made the subject of an exact electrometric investigation by Knüpffer, at the suggestion of Bredig. This reaction is better suited for a study of the reaction isotherm, since the solubilities of TlCl and TlSCN are not so very different from each other as are those of Ag_2SO_4 and AgCl, for instance. With an easy measurable proportion of Cl' to SCN' the e. m. f. of the cell passes through zero.

In order to test the relation between concentration and e. m. f., Bredig and Knüpffer used the following arrangement:

Tl	Solution of Cl' ..... Solution of SCN'	Tl	(IVv)
	1 Saturated with TlCl 2 Saturated with TlSCN	3	

The e. m. f. of this cell is not strictly proportional to the free energy of the reaction, because of diffusion potentials between the two aqueous solutions.

Let us investigate the manner in which this cell (IVv) can be converted into one of similar structure such as (IVu). This problem also can be solved by the intermediate-salt rule.

We imagine inserted at 3 a solid TlSCN as well as another insoluble rhodamid, such as PbSCN:

Tl	Solution of Cl′....Solution of SCN Saturated in TlCl Saturated in SCN′	PbSCN solid	TlSCN solid	Tl

In such a cell the Cl′ and SCN′ can now be mixed in one solution, and the saturated solution of TlSCN can be used in place of solid TlSCN, giving us:

Tl	Solution of Cl′ and SCN′ saturated and PbSCN	PbSCN solid	Solution saturated in TlSCN and PbSCN	Tl

Instead of PbSCN, another insoluble rhodamid might be used, so long as it is less soluble than the chloride in question.

It is seen that this arrangement is fully analogous to the cell (IVu), which on its side was derived from the cell with solid salts. It may be objected that a measurement with such arrangements offers no advantage over those formerly used. It was intended only to show that arrangements without transfer potential are possible even for cells such as those of Bredig and Knüpffer.

Such examples could be multiplied *ad libitum;* numerous other arrangements are possible.

CONCLUSIONS.

The new galvanic cells described in this paper give a general view of the diversified applicability of the forces at the phase limits for giving measurements of the free energy of reactions of all kinds. The examples could be considerably increased, if desirable.

The setting up of galvanic cells as here described is, as a rule, only possible with the help of at least one solid salt, which is in the current path. The inner resistance of the cells is therefore extraordinarily large, making the measurement of the e. m. f. difficult. This difficulty is not insurmountable, as is shown by exact measurements of the e. m. f. of such cells with solid salts made by Lorenz and Katayama.

It is to be expected that the simple relations between A and Q holding for such reactions, forming the foundation of the Nernst theory of heat, can thus be given a general confirmation. It should then be further possible to make more precise and to control in general the frequently uncertain calorimetric data of thermochemistry.

ABSTRACT.

It has been shown how galvanic elements can be arranged so as to measure, without transfer potential, the free energy of reactions between solid salts and metals or between solid salts alone. These cells are mostly characterized by containing solid salts in the path of the current.

If two reacting constituents are present in mutual admixture, the reaction can no longer be treated as "fixed," since osmotic forces then come also into play. But even for such cases suitable galvanic cells for measuring the free energy are described. To these belong, for instance, the formation of salt hydrates, in which it is almost always found that the resulting salt hydrate is considerably soluble in water, and in consequence a fluid mixture of salt hydrate and water enters into the reaction.

Further, new electrometric methods were given for chemical reactions of the kind described, in which the reacting constituents were present diluted by indifferent bodies. To such belong especially such reactions in which salts take part in practically completely dissociated dilute solutions. It could be shown in what way cells could be arranged for the measurement of reactions, avoiding the diffusion potentials, as, for instance, the reactions in the Bredig-Knüpffer cell.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

A RAILWAY TRACK CELL

By E. L. Marshall.

The subject of this paper is a primary cell of the wet type, which has been developed within the last decade to perform an unusual kind of service—a service which has been demanded by modern methods of railway signaling. Its predecessor in the same field was the gravity cell, a two-fluid cell in which the force of gravity keeps the heavier fluid separate from the lighter one.

Prof. Daniell is generally given the credit for having developed in 1836 the cell which later grew into the present gravity cell. Daniell's cell contained a porous-walled vessel for separating the two fluids, and consisted essentially of a copper cathode surrounded by a saturated solution of copper sulfate and a zinc anode surrounded by dilute sulfuric acid. Prior to this time primary cells had given but small amounts of current on closed circuits and were short-lived in service. However, by the application of copper sulfate as a depolarizer Daniell produced what he called a "constant" cell.

Daniell's "constant" cell became the gravity cell when the porous cup was eliminated and the sulfuric acid replaced by a dilute solution of zinc sulfate. In its present form (Fig. 1) the gravity cell has in the bottom of its jar a cathode of thin, narrow, vertical sheets of copper. A cast zinc anode in the shape of an annular ring is suspended near the top of the jar. The lower part of the electrolyte is concentrated copper sulfate solution and on top is poured a dilute solution of zinc sulfate. The lower specific gravity of the zinc sulfate solution prevents it from mixing with the heavier copper sulfate solution below. During the action of the cell zinc is dissolved from the anode, replacing copper in the copper sulfate, and this replaced copper is deposited upon the copper cathode. The top solution gradually becomes stronger with zinc sulfate, and, in order to prevent a weakening of the copper sulfate

solution below, solid copper sulfate is kept in the bottom, piled around the cathode. The popularity of the gravity cell has been due largely to its simplicity compared with the cells which preceded it. The materials necessary for renewals are reasonably cheap and fairly easy to obtain. A great many types of electrical apparatus have, at some stage of their development, made use of the gravity cell. In fact, it may be said that the gravity cell has

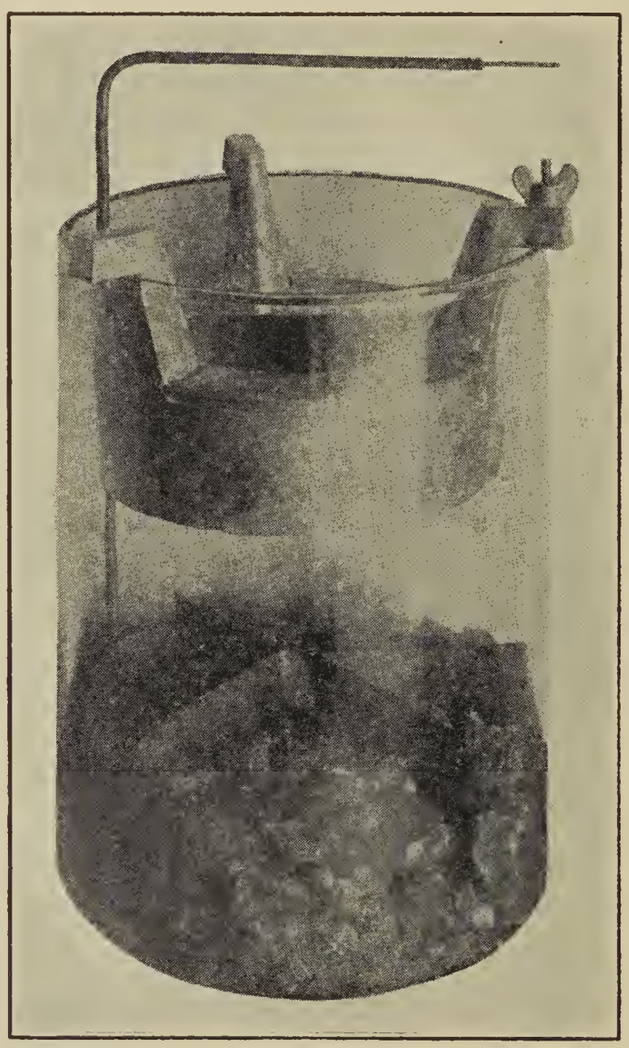


FIG. 1.

had more to do with the expansion of the field of electricity than any primary cell in use before the beginning of the twentieth century.

In the latter part of the nineteenth century great activity ensued along the line of automatically-operated signals to control and govern the movement of trains along railroad lines. Up to this time more or less signalling had been maintained by means of

local stations inter-communicating by telegraph, which was efficient for the amount of traffic at that time. However, as the amount and speed of traffic increased, the need for more efficient control and operation of signals arose. For this purpose there was worked out a method of signalling known as the automatic block system, which is still in use, though more or less changed. The automatic block system created the demand for the cell which will be described.

First, we shall discuss the general electrical equipment for automatic block signalling. With either single-track or multiple-track roads the layout consists essentially of two electric circuits, the signal circuit and the track circuit (Fig. 2). The function of the signal circuit is to operate the visible signal arm and thus convey to the engineman in the cab of his moving train all necessary information about the blocks in front of him. This signal circuit includes a motor for moving the signal arm, a battery to supply current to the motor, and relays which control the circuit so that the motor operates at the proper times. The battery may consist of low-resistance primary cells or of storage cells.

The track circuit is of more interest, because it brings us directly to the cell which is the subject of this paper. The railway track cell we refer to was designed particularly for service on the track circuit. The track circuit consists of a relay, a section of the railway track, and a battery. The electric current from the battery flows through the 4-ohm magnetizing coils of the relay, thus holding up the armature. The signal circuit mentioned above is so wired to the armature of this same relay that when the track circuit current ceases to flow through the relay's coils and allows the armature to fall away, the signal circuit is opened and the signal moves to danger position by gravity.

The section of railway track in the track circuit includes both sets of rails of one track for a distance of one block. A block is the space between two adjacent signal standards, which we can see by the side of any railway track, and it varies in length from one-half mile to one mile. The relay is at one end of this track section and the battery at the other. Between the battery and the relay the current flows down through one set of rails

and back through the other. The battery is required to furnish current to the circuit at all times and under normal conditions, *i. e.*, when there is no train in the block, the current supplied is used up in three places:

1. In the relay.
2. In the external circuit, mostly of rails.
3. As shunted current or leakage from one set of rails through the ties or ballast across to the other set of rails.

The amount of this current leakage between the sets of rails depends upon the nature and condition of the roadbed.

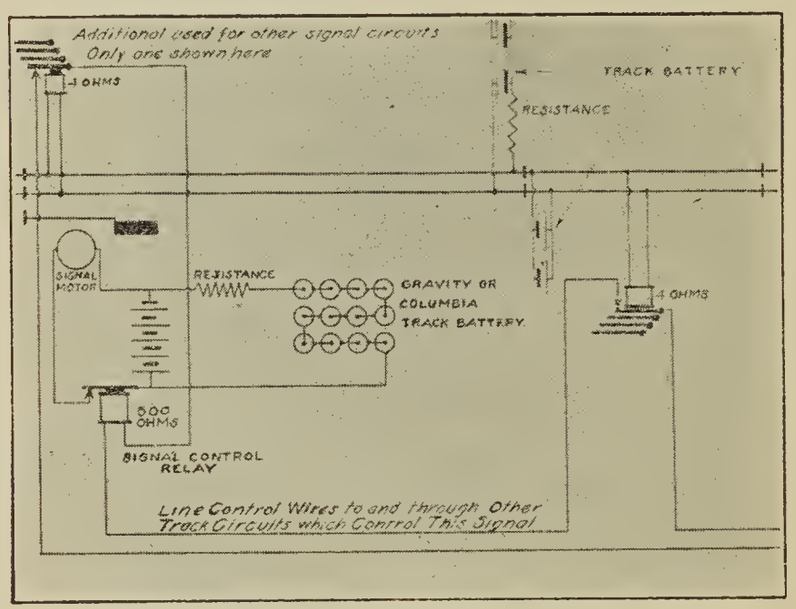


FIG. 2.

Whenever a train is in the block, the current from the battery follows the rails until it reaches the train and there it is shunted from one set of rails to the other through the wheels and axles of the train, instead of passing further along the rails and through the coils of the relay. In other words, the relay coils are de-energized, the armature falls away, the signal circuit is opened, and the signal goes to danger position. The resistance between the sets of rails through the trucks of the cars is so small that the battery is short-circuited as long as the train is in the block. It is evident then that the hard work of the battery comes when a train is in the block, and that the life of a battery is dependent to a considerable extent upon the number of train movements per day.

Some essential features of a cell which can be used successfully on track circuits are:

1. Low current on short-circuit.
2. Constant voltage on closed circuit.
3. Large capacity.
4. Small fluctuations due to variations in temperature.

During the early stages of automatic signalling the gravity cell was the only one used, for it more nearly fulfilled the requirements than any cell then on the market. Its short-circuit current is low, because of its high internal resistance. Its voltage is constant on closed circuit. Its capacity, however, is not large, for about once a month either the zinc has to be cleaned or the elements have to be renewed. The range of temperature within which it will work is limited by the fact that the electrolyte freezes at a temperature close to the freezing-point of water.

In 1903 experimental work was carried on in an endeavor to develop a cell for track circuit work which would have all four of the essential features noted above. The Lalande type of cell was chosen as offering the most promising opportunity. It is a single-fluid cell with a zinc anode, a cathode of copper oxide and an electrolyte of caustic potash or caustic soda solution. When the cell is delivering current, zinc is dissolved and oxygen given up by the depolarizing cathode of copper oxide. The oxidized zinc remains dissolved in the electrolyte, combined with the sodium hydroxide in the form of sodium zincate.

There had already been perfected a Lalande cell with a low internal resistance and consequently a high amperage on short-circuit. For most classes of service a cell's value and efficiency are improved by decreasing its internal resistance. But our problem was a peculiar one. It was necessary to get high internal resistance, or apparent inefficiency, in the cell which would serve well on track-circuit work—which would not eat up its life blood at an excessive rate whenever a train passed through the block it was guarding.

One method tried for obtaining a high internal resistance in a Lalande cell was to place a perforated porcelain plate between the zinc anode and copper oxide cathode. The plate acted merely as a mechanical obstruction to the circulation of the electrolyte and to

the passage of current through the electrolyte. It increased the internal resistance; but the cell was not as efficient as the form finally perfected, the Columbia track cell (Fig. 3). The high internal resistance is obtained in this cell by merely separating the two electrodes a long distance apart in the electrolyte, no added piece being used for the purpose. In fact, in number of parts and ease of assembling it is the simplest primary cell now on the market. Its parts consist only of the following:

FIG. 3.

1. The glass jar.
2. The electrolyte with its oil covering.
3. The copper oxide cathode.
4. The zinc anode.

The glass jar is 6 in. (15 cm.) in diameter and 8 or 10½ in. (20 or 27 cm.) high, according to the capacity of the cell. The glass in the jar is of a special quality designated as "heat-resisting," so called because it will stand rapid and extreme changes of temperature without breaking. This property is desirable because in mixing up fresh electrolyte the dissolving of solid caustic soda in water produces a very hot solution. Our heat-resisting test which these jars must pass is the ability to hold

inside the jar a caustic soda solution at 105° C., the jar being surrounded by a water-jacket at 15° C., without developing a single crack. Glass jars are preferable to porcelain ones because they permit a clear view of the elements within the cell.

For the electrolyte, caustic soda is used in preference to caustic potash, because it is cheaper and more available in the market. The solution used has a specific gravity of 1.25 (29° Bé.) This is largely in excess of the amount required to form sodium zincate with all the zinc dissolved, but is necessary to hold in solution the sodium zincate after it is formed. The function of the layer of mineral oil on top of the electrolyte is to prevent the evaporation of water from the solution and to prevent the solution from creeping up the side of the jar or the wires.

The depolarizer consists of flaky copper oxide, which is poured into the bottom of the cell after the solution has been made up. Underneath the copper oxide is a disc of tin plate, to which is riveted a rubber-covered copper wire that passes up thru the center of the electrolyte and emerges from the cell as the positive terminal. The disc provides intimate contact between this terminal and the copper oxide cathode. As the function of the copper oxide is to supply oxygen, all oxide used in this cell has to pass an analytical test, which shows whether it contains sufficient available oxygen.

The zinc anode is circular in form, and is suspended in the electrolyte just below the surface by three short wires bent over the top edge of the glass jar. A fourth and longer insulated wire serves as the negative terminal of the cell. There are two types of circular zinc anodes used. One is made of a long, narrow piece of sheet zinc rolled into form, and the other is made by being cast into the final shape. A small amount of mercury in the zinc is needed to prevent local action. For the cast zinc mercury is alloyed with the zinc before the anode is cast; but with the rolled zinc the surface is thoroly amalgamated by dipping the zinc in mercury after it has been rolled and the wires riveted on.

The reduction of the black copper oxide to red copper during the action of the cell provides a valuable visible indication of the state of exhaustion of the cell. The Columbia Track Cell is the only primary cell which has this important property. An excess

of zinc over the amount used in the chemical reaction is always necessary to provide mechanical strength for the anode. If there is an excess of copper oxide, the electrolyte becomes exhausted first. Such a condition is manifested by the deposition of insoluble sodium zincate crystals on the zinc anode, which is finally covered completely with the crystals. But in the cell mentioned the elements are so proportioned that the copper oxide is all used up just before the solution becomes exhausted. Thus it is possible, by watching the decreasing band of black oxide showing around the outside of the cathode, to predict a couple of weeks ahead of time the probable date when a cell should be renewed.

The initial readings on this railway track cell are 0.9 volt on open circuit and 2.0 to 2.5 amperes on short-circuit. In ordinary service delivering 0.2 ampere current, which is equivalent to being closed on a circuit of 3 ohms resistance, it averages about 0.6 volt. The internal resistance is about one-third ohm. The cell designed for an 8-inch (20 cm.) jar has a capacity of 400 ampere-hours and the one for a 10½-inch (27 cm.) jar gives 600 ampere-hours. In the usual types of service (at 0.6 volt) the total energy output would amount to 240 watt-hours for the one and 360 watt-hours for the other. The latter amounts to one-half a horsepower-hour or 1,230 B. T. U. (318 Calories). For the ordinary track circuit the most efficient battery consists of two cells connected in parallel. The minimum battery voltage needed on the circuit is 0.4 volt.

Returning to the four essential requirements for a track circuit cell, we find that our improved type of Lalande Cell fulfills them all:

First, it gives a low current on short-circuit, on account of its high internal resistance.

Second, it maintains a constant voltage when closed on the track circuit.

Third, with the large capacity of 400 to 600 ampere-hours it lasts from three to six months on average track circuits.

Fourth, its ability to give current at very low temperatures makes it serviceable under all conditions of weather.

In conclusion, the railway track cell just described is superior to the gravity cell for track-circuit service in the following points:

1. It has a larger capacity. It has to be renewed only once in three to six months, while the gravity cell needs attention every month.

2. This increased capacity reduces the cost of maintenance.

3. It is simpler in construction, being a one-fluid instead of a two-fluid cell.

4. The electrolyte will not freeze in any temperatures encountered in this country, while the gravity cell has to be kept underground below the frost line to prevent freezing.

5. And last, but not least, the visual indication of the copper oxide gives one positive information of the approaching exhaustion of the cell.

Research Laboratory of National Carbon Co.
Cleveland, Ohio.
March, 1914.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

EXPERIMENTS ON WHITE LEAD.

By R. Stuart Owens.

The work was undertaken to determine, if possible, in what way and to what extent the character of precipitated white lead varied with the conditions of precipitation. The Dutch process for making white lead seems still to be the standard one, although it is slow and consequently ties up a large amount of capital. Holley[1] cites the Carter process, the Rowley process and the Matheson process as rapid processes which are on a commercial basis. No electrolytic process seems to be a commercial success as yet, though the rapidity and control of corrosion is a strong argument in favor of an electrolytic process. The difficulty is that the electrolytic white lead is crystalline and consequently lacks covering power. It also requires a large amount of oil. This latter difficulty is said to be overcome by a process patented in 1907 by Mr. E. A. Sperry, the substance of which is as follows:

"For the electrolytic production of a lead pigment a previous electrolytic treatment of the lead is stated to be highly advantageous, whereby the lead is used as anode and deposited on the cathode, the cathode product being then used for making the pigment. For example, white lead produced electrolytically absorbs as high as 20 drops of oil per gram to bring it to a standard paste, whereas, by using the cathode product of the first electrolysis as anode in the second, the particles may be rendered harder, thus forming crystals which work smoother under the brush, as well as possessing other qualities which make it more desirable. Probably the most distinguishing feature is that the white lead so formed is said to bring down the oil absorption to between 3 or 4 drops per gram, a reduction of something over 75 percent in the amount of oil required."

[1] The Lead and Zinc Pigments, pp. 74, 85, 101 (1909).

It is difficult to see how the precipitation of an electrolytically formed lead salt can depend on the physical characteristics of the lead anode, though the efficiency of corrosion might be affected. Unless the first electrolysis caused a refining of the lead, it is extremely improbable that the results are due to the alleged cause.

White lead is a definite compound,[2] $(PbCO_3)_2PbO_2H_2$, and the commercial white leads do not vary much from this composition. Experiments were therefore made on the precipitation of lead carbonate, lead hydroxide and basic lead carbonate, from solutions of varying concentrations and at varying temperatures. Solutions of sodium hydroxide, sodium carbonate and lead acetate were made up of concentrations varying from normal to sixty-fourth normal, the word normal being used in the sense of equivalent concentration and not of molecular concentration. For this work a normal solution of sodium carbonate or caustic soda contains 23 grams of sodium to the liter, and a normal solution of lead acetate contains 103.5 grams of lead to the liter. Strictly speaking, only the normal solutions were made up accurately, the others being prepared by adding 500 cc. water to 500 cc. of the preceding solution. The error due to contraction or expansion is presumably negligible for work of this type, and has been so considered.

It seemed desirable to find out what variations in crystal size might be expected. Since moderately high concentrations of the precipitating agents and moderately low temperatures are favorable in general to the production of small crystals, precipitations were first made from normal solutions at room temperature and from N/16 solutions at higher temperatures. The precipitated crystals were examined in the mother liquor under the microscope, using an eye-piece with a scale. The data are given in Table I.

TABLE I.

Precipitate	Solution	Temperature	Diameter
Lead carbonate	N/1	20°	0.0010 mm.
Lead carbonate	N/16	80°	0.0023 mm.
Lead hydroxide	N/1	20°	0.0010 mm.
Lead hydroxide	N/16	80°	0.0375 mm.

[2] Hawley: Jour. Phys. Chem., **10**, 654 (1906).

The lead carbonate precipitates varied in a ratio of about one to two, and the lead hydroxide precipitates in a ratio of nearly one to forty. A series of runs was therefore made. The solutions were all precipitated by placing 50 cc. lead acetate solution in a beaker in a constant temperature water bath and adding an equal volume of the corresponding hydroxide or carbonate solution to it. During precipitation the solutions were stirred by an electrically driven stirrer. The importance of this has been emphasized by Free.[3] The data for lead carbonate are given in Table II.

TABLE II.

Lead Carbonate.

Solution	Temperature	Diameter in mm x 1000
N/1	20°	1.0, 1.2, 1.0
N/2	20°	1.4, 1.4
N/4	20°	1.8, 1.8
N/8	20°	2.
N/8	60°	2.
N/16	20°	2.
N/16	74°	2.
N/16	80°	2.3
N/32	20°	2.3
N/32	45°	2.4
N/32	70°	2.5
N/64	70°	Milky solution

The particles from the N/2 solutions settled more rapidly than those from the N/1 solutions. The particles from the N/4 solutions settled rapidly and appeared as rounded masses. From the N/8 solutions rounded, egg-shaped masses were obtained. With N/16 solutions a very uniform field of round-shaped particles was obtained at 20°, while at 70° and 80° the particles were slightly transparent. With N/32 solutions at 20° and 45° a milky liquid was obtained, which required over twenty-four hours to clear, rounded, globular-shaped particles settling. When precipitated at 70° the solution cleared in about twelve hours, rounded, globular-shaped particles separating. With N/64 solutions no precipitates were obtained from the slightly milky solutions when allowed to stand for three days at room temperature, regardless of the temperature of precipitation.

These results are in harmony with those obtained by Free[4] in

[3] Jour. Phys. Chem., **13**, 128 (1909).
[4] Jour. Phys. Chem., **13**, 130 (1909).

his work on lead chromate. Free found that "in the very dilute solutions lead chromate remains in colloidal solution for several days," and that the largest crystals are obtained in hot and dilute solutions. The mean size of the particles is, of course, given by the amount of lead carbonate in excess of that required to saturate, divided by the number of particles. If the number of particles decreased proportionally to the supersaturation, the size of the particles would remain constant. If the number of particles falls off more rapidly than the supersaturation, the size of the particles will increase with increasing dilution of the reacting solutions; the size of the particles will decrease if the number falls off less rapidly than the supersaturation. In concentrated solutions the precipitation takes place so rapidly that the crystals do not have time to grow, which is another way of saying that the number of nuclei is relatively high. With more dilute solutions we usually say that the crystals have time to grow; but we could equally well say that there are relatively fewer nuclei formed. With very dilute solutions the crystals are not large, because there is nothing left in the solution after the nuclei are formed. In other words, the number of the nuclei does not decrease anything like as rapidly as the supersaturation. This is not inconsistent with the fact that the mineralogists obtain crystals of insoluble substances by allowing dilute solutions to diffuse together slowly. A colloidal solution may perfectly well give rise to relatively large crystals in the course of sufficient time, because the very fine particles are more soluble than the relatively large crystals. On the other hand, it is not yet clear how one could predict that the relative number of particles will first decrease and then increase with decreasing supersaturation. It is not at all what one would expect from Tammann's experiments on the behavior of supercooled liquids.

The data for lead hydroxide are given in Table III.

With N/2 solutions, rounded masses of lead hydroxide were obtained. With N/4 solutions a mixture of needles and skeletons were obtained at 20°; at 48° a uniform field of crosses was obtained; and at 70° a less uniform field, composed chiefly of crosses with pointed ends. With N/8 solutions there were only crosses at 20°, but they were filled out better than with the more concentrated solutions. At 66° there was a slightly yellow

precipitate, and the crosses were nearly filled out, so that there was a gradual gradation from crosses to lop-sided cubes. At 47° the yellowish precipitate was lighter than at 66°. The crystals were crosses of varying sizes, but only a few were nearly filled out. At 33° there were hardly any well-formed crystals, mostly all being skeletons. At 28° there were no cubes. Both at 28° and 33° there was no yellow precipitate. With N/16 solutions at 20° the crystals were all long, yellowish needles of different sizes. At 60° there was a distinct yellow color but no crystal needles. With N/32 solutions at 20° a whitish precipitate was obtained, but no distinct crystals were noted.

TABLE III.

Lead Hydroxide.

Solution	Temperature	Diameter in mm x 1000
N/1	20°	1.0, 1.0
N/2	20°	1.5, 1.5
N/4	20°	7.5 (1.5 wide)
N/4	48°	12.5
N/4	70°	15.
N/8	20°	25.
N/8	66°	17.5 (crosses)
N/8	66°	12.5 (cubes)
N/8	47°	50—7.5
N/8	33°	30 (white)
N/8	28°	30 (white)
N/16	20°	37.5 (needles)
N/16	60°	37.5 (no needles)
N/32	20°	whitish precipitate

The general conclusions from the experiments given in Tables II and III are as follows:

1. The size of the particles of the precipitate varies with the conditions under which it is formed.

2. As with other substances, larger particles of lead carbonate and of lead hydroxide are obtained from hot, dilute solutions than from cold, concentrated ones.

3. The lead carbonate could not be obtained as definite crystals, the prevailing form being rather that of an egg. The globules of the lead carbonate thus produced appeared translucent under the microscope.

4. The lead hydroxide was obtained in definite crystalline

form, varying from needles to what appeared to be lop-sided cubes. The size of the particles could be varied much more than in the case of the lead carbonate.

Some years ago it was pointed out[5] that one could start with a coarse and a fine lead hydroxide and a coarse and a fine lead carbonate and could combine these in four different ways, thereby getting the possibility of four different white leads. This experiment was tried, starting with lead hydroxide and lead carbonate precipitated at 20° from N/1, N/8 and N/16 solutions. The moist precipitates were mixed in the proper proportions, covered with dilute sodium acetate solution, stirred occasionally, and left at room temperature until equilibrium was reached. Tests were made from time to time to see whether any particles of the original substances remained. Equilibrium was always reached inside of twenty-four hours. All possible combinations were tested.

The resulting particles of white lead did not seem to possess a definite crystalline form, and were all of the same size, shape, etc., irrespective of the size of the original reacting particles. The average size of the particles was 0.0015 mm.; while most of them were rounded, a good many were elliptical, and all appeared translucent. The most probable explanation for this result is that the solid lead carbonate and lead hydroxide did not react directly to any appreciable extent, and that the white lead was formed by the interaction of lead carbonate and lead hydroxide dissolved in the dilute sodium acetate solution. Experiments were also made with 5N, N/1, N/5 and N/50 sodium acetate solutions at 20°, with practically the same results. At higher temperatures equilibrium was reached more rapidly; while there seemed to be a slight difference in the size of the particles, the amount of the change could not be estimated. This is probably due to the fact that the higher temperature and the more rapid reaction counterbalance each other.

It was next decided to mix the sodium hydroxide and the sodium carbonate solutions in the ratio of one to two, and then to pour this mixed solution into an equivalent lead acetate solution, varying the concentrations and the temperature. The data are given in Table IV.

[5] Bancroft: Trans. Am. Electrochem. Soc., **14**, 150 (1908).

TABLE IV.

White Lead.

Lead acetate solution	Diameter in mm x 1000		Appearance
	20°	98°	
N/1	1.25	0.8	Rounded and translucent
N/2	1.5	1.0	" " "
N/4	2.0	1.5	" " "
N/8	2.0	1.6	" " "
N/16	1.8	1.6	" " "
N/32	0.2	1.6	" " "
N/64	0.2	0.2	" " "

Experiments were made only at the two extreme temperatures because it was thought that sufficient data would be obtained thereby for present purposes. It is not clear why the particles should be smaller at the higher temperature than at the lower. It is possible that the agglomeration at the higher temperature has given rise to a denser form. The time at my disposal did not permit of a further study of this unexpected phenomenon. The data show that the average size of the particles of white lead can be varied from 0.0008 mm. to 0.0020 mm. without having recourse to solutions more dilute than N/16. While this change in size is not very large, it shows the possibility of making a number of white leads having different physical properties, though identical in chemical composition.

The next step was to determine which size of particle was best for commercial purposes. Owing to lack of time, this point was not worked out thoroughly. Covering power, durability, oil absorption and the ease with which the pigment may be worked under the brush should be considered. The oil absorption was first tested on the laboratory scale; working under the brush was then tested, and a few pieces of wood were painted so as to obtain some idea of the covering power; but nothing whatever was done in the way of testing durability.

Correspondence as to the best method of determining oil absorption brought out very little except advice to consult a practical painter. Anybody who has had any experience with a so-called practical painter knows that it would have been an absolute waste of time to follow this advice. Consequently a

method of determining oil absorption was worked out which had the merit of giving very interesting results and which probably possessed a fair relative accuracy. Of course, no method can be called accurate which depends in such a way on the sense of touch. The method employed was to use a convenient receptacle, into which any known weight of the dried white lead was placed. The linseed oil was allowed to run in from a burette until a certain consistency was reached. In this work a three-inch agate mortar and pestle were used. Five or 10 grams of white lead were placed in the mortar, and the oil was allowed to drop into the pigment, with which it was carefully mixed. The process was continued through the granular state until the mixture finally became pasty and sticky. When the mass became so sticky that the mortar could be lifted by the pestle adhering to the paint, the cubic centimeters of added oil were noted, as this seemed to be a fairly accurately reproducible end-point. This end-point differs very much from that selected by the painter, but each end-point could be expressed in terms of the other by anybody who knew what the painter's end-point was.

The data are given in Table V.

TABLE V.

Oil Absorption with Precipitated White Lead.

Size of crystals in mm x 1000	c.c. oil used	Pigment in grams
2.2	1.1	5
2.0	1.0	5
1.6	0.9	5
1.4	0.85	5
0.8	0.55	5

These results show that the amount of oil needed does not increase proportionately to the size of the particles; but it also shows conclusively that there is a marked difference in the amount of oil needed to produce the given end-point.

The following qualitative observations were made on the covering power as affected by size of particles. Paints made from the larger particles and from the smaller ones were applied to pieces of wood previously painted with a black of unknown com-

position. After drying for twenty-four hours the pieces of wood were examined, and it was found that the paint made from the smaller particles was far superior to that made from the larger ones. A second coat of paint was given to the piece of wood which had been painted with paint made of the larger particles; but, after drying, the coating was thought still to be inferior to that on the other sample. It was therefore decided that one coat of paint made from the smaller particles was certainly superior to two coats of the paint made from the larger particles. The reason for this difference is perhaps to be found in the fact that the pigment precipitated from the lead acetate solution consisted of translucent rounded particles which seemed to possess no definite crystalline form. In a particle like this the covering power is due chiefly to the rim of the globule, and consequently the covering power will be less the greater the relative proportion of translucent center.

As for the property of working under the brush, it can only be stated that the smaller particles seemed to work better. A definite statement could be made only after experiments by an expert with much larger amounts of pigment.

Since the small particles make the best pigment so far as these tests are concerned, it seemed desirable to make a few observations on commercial white leads. On examination of some pigments made by processes similar to the Dutch process, it was found that the product varied considerably in the size of the particles contained, but that the average run was probably about 0.0014 mm. It should be noticed that it is not necessarily desirable to have the particles of uniform size. Approximately circular particles will pack more closely and consequently will have greater covering power when of two or more sizes than when uniform.

Products obtained from outside sources may be given as follows:

Eagle White Lead Company: Average size 0.0022 mm.; composed of rounded and fragmental pieces.

Acme White Lead Company: Even product, averaging about 0.0024 mm.

Matheson White Lead Company: Average size 0.0022 mm.; mostly well-rounded masses.

Carter White Lead Company: Average size 0.0018 to 0.0020 mm.; rounded particles, uniformly smaller than other varieties examined.

National White Lead Company: Average size 0.0020 mm.; a very scaly product of irregular shapes.

It was very interesting to note that, when equal volumes were placed in the sample bottles, the bottles containing the smaller and the larger crystals could be differentiated by weight alone.

The last experiment was to make some white lead electrolytically on the laboratory scale. The Woltereck and Luckow methods were taken as fairly typical. Data for the experiments were obtained as far as possible from the United States patents.

1. *Woltereck Patent,* No. 589801.

Electrolyte contains 10–15 percent of a mixture of 80 parts CH_3CO_2Na and 20 parts $NaHCO_3$.

Carbon dioxide introduced at bottom of vessel; solution stirred.

Lead electrodes; current density one ampere per square decimeter.

Results: Much oxide of lead thrown down with the white lead; anode badly pitted.

Size of crystals = 0.002 mm.

2. *Luckow Patent,* No. 627662.

Electrolyte contains 0.3–3.0 percent of a mixture of 80 parts $NaClO_3$ and 20 parts Na_2CO_3.

Sodium carbonate added from time to time; solution stirred.

Lead electrodes; current density 0.5 ampere per square decimeter.

Results: Anodes in fairly good condition.

Size of crystals = 0.0022 mm.

From these two tests it will be seen that the sizes of the crystals are what one would expect from slow precipitation. The fact that the particles are much the same size as those obtained by the rapid processes does not prove that the electrolytic white lead is as good as the other, because no tests were made on the density, the oil absorption, etc. These experiments do prove that these two electrolytic methods are not run under conditions which give the best precipitate of white lead.

The general results of this paper are:

1. Lead hydroxide can be precipitated with a definite crystalline form, and the size of the crystals can be varied between rather wide limits.

2. Lead carbonate was not precipitated in any definite crystalline form. It is probable that the particles consist of aggregates of very small crystals. The size of the particles can be varied between narrow limits.

3. When a mixture of particles of lead carbonate and lead hydroxide are allowed to stand together under a sodium acetate solution, the particles of white lead have the same size, no matter what the size of the particles of the reacting salts.

4. When a suitable mixture of sodium hydroxide and sodium carbonate is added to a solution of lead acetate, white lead is precipitated, and the size of the particles can be varied between rather narrow limits.

5. White lead thus prepared does not show any definite crystalline form; it seems to consist of rounded translucent particles.

6. Rapid precipitation gives smaller particles, and slow precipitation gives larger particles.

7. The commercial samples and those produced in the laboratory by electrolytic means had particles corresponding in size to those obtained by slow precipitation.

8. The oil absorption, as tested, is much less with small particles of white lead than with the larger particles.

9. The paint made from a pigment consisting of smaller particles was superior to that produced from a pigment consisting of larger particles.

10. Uniformity in size of particles is not necessarily an advantage in a paint.

The experimental work was done in 1910, but publication has been delayed. The work was suggested by Professor Bancroft, and was carried out under his supervision.

Cornell University.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

A MICROSCOPIC STUDY OF ELECTROLYTIC IRON.

By Oliver W. Storey.

The electrolytic refining of iron was first carried out successfully ten years ago by Prof. C. F. Burgess at the Chemical Engineering Laboratories of the University of Wisconsin.[1] Since then, several thousand pounds of iron have been refined. In its manufacture a large variety of forms of cathode deposits has been produced, varying from dense to porous, and from smooth to nodular iron. The work presented in this paper was undertaken to study the different kinds of deposited irons and also to study the effect of heat treatments upon them. The author is indebted to Prof. C. F. Burgess, of the Northern Chemical Engineering Laboratories, for his co-operation in this research.

The refining of iron is carried out at present in stoneware tanks, each containing three sets of anodes, connected in parallel, between which are placed the two cathode sheets, allowing deposition to take place on both sides of the latter. The anodes first used were Swedish bar iron, though later American Ingot Iron has been used as a purer grade of raw material. With a current density of about ten amperes per square foot and an electrolyte consisting of an aqueous solution of iron sulphate and ammonium chloride the deposition proceeds uniformly.

A typical analysis of the refined iron follows:

	Single Refined	Double Refined
Sulphur	0.001%	none
Silicon	0.003	0.013%
Phosphorus	0.020	0.004
Manganese	none	none
Carbon	0.013	0.012
Iron	99.963	99.971
Hydrogen	0.083	0.072

The double refining is accomplished by using an electrodeposited material as anode.

[1] Burgess and Hambuechen, Tr. Am. Electrochemical Society, **5**, 201 (1904).

The electrodeposition of iron presents difficulties not unlike those present in the deposition of various other metals. By varying the factors such as current density, temperature, circulation of solution, composition of electrolyte, gases and impurities in the electrolyte, and thickness of deposit, various kinds of deposits may be obtained.

The microstructure of electrolytic iron has been the subject of a paper presented before this society by Professors C. F. Burgess and O. P. Watts.[2] This described the various kinds of deposits obtained and also the conditions producing these deposits. Attention was also called in this paper to the striking similarity of the structures of electrolytic iron to the structures of certain minerals as formed by nature. This similarity was especially noticeable with manganite, hematite and limonite.

Different types of deposits are shown in Figs. 1, 2 and 3. Fig. 1 shows a fracture of a hard, dense deposit illustrating a characteristic tooth-like growth. These nodular deposits may be separated from the main body of the metal by hitting them a sharp blow with a hammer. Cavities, sometimes one-half inch in depth, are formed. A group of nodules or teeth resulting from the breaking up of an iron cathode are shown in Fig. 4.

The deposit shown in Fig. 2 illustrates the usual fine grained deposit which is more fibrous in nature than that of the nodular iron shown in Fig. 1.

Fig. 3 shows a coarse, porous, crystalline deposit. The dense structures of Figs. 1 and 2 are entirely absent but instead a series of layers of iron is shown. The fine crystals shown at the bottom of the cathode gradually grow into coarse crystals at the top.

All of these deposits show lines parallel to the starting sheet indicating surfaces of cleavage. These cleavage surfaces are produced when some interruption or change in the deposition occurs. In the denser deposits the planes of cleavage are not as apparent as in the porous structure of Fig. 3. In this deposit layers of iron may be easily removed with a pen knife.

That the deposits obtained are of a variable structure is illus-

[2] A Microscopic Study of Electro Deposits, Tr. Am. Electrochemical Society, **9**, 229 (1906).

trated in Fig. 5. Some of the layers are dense and hard as is shown by the slight amount of etching while others are porous and easily etched.

When a metal solidifies from the molten state, the growth of crystals commences from nuclei distributed at random throughout the mass. The individual crystals grow outwards from these nuclei (usually by means of dendrites) until the sides of the mould or other crystals prevent further growth. In this manner the neighboring crystals found in metals solidified from the solid state usually are of different orientation. The growth of a metal when deposited by means of the electric current is different from the above case. The metal is first deposited on a starting sheet and the growth of it can be in only one direction—perpendicular to the surface of the starting sheet.

A microsection of the electrolytic iron shown in Fig. 3 in a plane perpendicular to the starting sheet gave the structure shown in Figs. 6 and 7. Fig. 6 shows the finer crystals at the starting sheet while Fig. 7 illustrates the coarseness of these crystals at the outside of the deposit, which was 5/16-inch (8 mm.) in thickness.

The crystal growth of Fig. 6 presents a peculiar fan-like appearance. The heavy line shown in the photograph is the result of a marked interruption in the deposition. The finer black lines which are about one-half inch apart and parallel to the heavier line are the result of slight interruptions in the deposition. The heavier lines are cleavage planes along which the layers of iron easily separate.

The growth of the crystals is again illustrated in Figs. 8, 9 and 10. Fig. 8 shows the microstructure of the cathode next to the starting sheet and parallel to it. This deposit when resolved under high powers shows a grain structure. Fig. 9 represents Fig. 8 at a higher magnification. The outside of the cathode has a coarse grain structure as illustrated in Fig. 10.

A more common form of deposit is shown in Fig. 11, which is a modified form of the deposit of Fig. 6. The black spots are probably cavities due to gases or other occlusions. The structure of the exterior of this cathode is illustrated in Fig. 12.

The interesting feature of Fig. 12 is the spider web appearance

of some of the crystals. Müller,[3] in his work on electrolytic iron, refers to this peculiar structure and shows a web with five sections. The author has been able to find such areas with both five and six sections, the latter being more frequent.

Fig. 13 is a micrograph of a dense though coarse deposit. The crystals in the fractured deposit were plainly visible to the naked eye and were often ⅛ inch in length. No interruptions had occurred in this deposit and the crystals grew to large sizes.

The microstructure of a dense deposit which is not nodular is shown in Fig. 14. The tendency to form well defined crystals is suppressed and only an indication of these crystals is present. The exterior of the cathode deposit shows a well defined granular structure. See Fig. 15.

The microstructure of the dense deposits resulting in the nodules of Fig. 4 and the nodular deposit of Fig. 1 differs from the crystalline deposits previously shown. The polished and etched surface of such a dense section is shown in Fig. 16.

A large nodule formed in the interior of this deposit may be distinctly seen, while a band of less dense deposit is visible at the top of the specimen. The microstructure of this section is seen in Fig. 17 while a part of the dense portion showing the boundary between two nodules is shown in Fig. 18. It was impossible to develop a crystal structure in this iron.

MICROSTRUCTURE OF HEATED ELECTROLYTIC IRON.

In their paper, C. F. Burgess and O. P. Watts,[4] showed that electrolytic iron, upon heating to 1,000° C., assumed the structure of ordinary iron, that is, it became granular. It was desirable to know at what temperature this change took place and what effect the liberation of hydrogen had upon the structure.

Electrolytic iron, as deposited, possesses peculiar properties. It is extremely brittle and dissolves with ease in acids, being more soluble than zinc.[5] The brittleness is probably due to the presence of hydrogen, either occluded or combined with the iron.

[3] Metallurgie, 1909, p. 145.

[4] A Microscopic Study of Electro Deposits, Tr. Am. Electrochemical Society, **9**, 229 (1906).

[5] Burgess and Engle, Tr. Am. Electrochemical Society, **9**, 199 (1906).

Upon heating electrolytic iron to between 500° and 600° C., a large amount of hydrogen was given off and the iron became ductile and more resistant to acid attack. Upon examination of the iron after heating for one hour at 600° no apparent change in the crystalline structure had taken place. Specimens heated for one hour at 700°, 800°, 850° and 875°, showed no change which could be detected by the microscope. By heating specimens at 910° to 915° C. for one hour the crystalline structure of the deposited iron had changed completely to the grain structure of ordinary ferrite.

This phenomenon occurs at the A_3 point in iron where a known allotropic transformation from gamma to non-gamma ferrite takes place. A change of the crystal form occurs and explains the cause of the change of the electro-deposited iron to the ordinary grain structure.

In this work the determination of change of structure was made upon a section perpendicular to the cathode surface. The close resemblance of the cathode surface to the ordinary grain structure did not allow a close determination of any change to be made. On the other hand, any difference in structure of the perpendicular surface could be detected.

For the further investigation of this phenomenon two varieties of electrolytic iron were used, fine and coarse. The fine electrolytic iron was dense and finely crystalline. Fig. 19 shows a micrograph of this structure. The coarse material was porous and the structure is shown in Figs. 6 and 7. In one set of experiments the specimens were annealed after heating at a constant temperature in the furnace and in the other were quenched in water.

An electrically heated tube furnace was used. The temperatures were measured by a base metal thermocouple correct to within 2°. The furnace atmosphere was oxidizing and a scale formed on all specimens. A list of experiments with results follows. All specimens were etched with picric acid:

1. Heated at 900° for 15 minutes and quenched.

a. Fine deposit; first changes in structure occur. See Fig. 20. The dense white bands of crystals of Fig. 19 have developed into several large grains while the porous dark bands have separated

into fine grains of ferrite as seen in the areas adjacent to the coarse grained white band.

b. Coarse deposit; no noticeable change in structure.

2. Heated at 900° for two hours and quenched.

a. Fine deposit; Fig. 21. A few traces of the old structure remain. The porous areas have been broken up into well defined fine grains while in the denser areas the coarse grains of Fig. 20 have divided into finer grains. The specimen appears to be breaking up into finer grains though Fig. 20 showed some that were coarse.

b. Coarse deposit. Fig. 22. The first breakdown of the crystalline to the granular structure is taking place. The change appears sluggish in comparison to the fine deposit. The entire surface has not changed. As seen in Fig. 22, fine grains are forming but these can only be found where a fine crystal structure had existed and are prominent at the base of these crystals. At the coarse end of the crystals no traces of a grain formation are found.

3. Heated at 910° to 915° for one hour and cooled in furnace. Only the coarse deposit was used.

a. Coarse deposit. See Fig. 23. The crystalline structure has changed entirely to the grain structure. Though traces of the old crystal outlines remain the grain boundaries are apparently not influenced by the crystal boundaries. The grains are several times as large as those obtained with the fine structure of Fig. 21.

4. Heated at 925° for five minutes and quenched.

a. Fine deposit. The entire specimen has become fine grained with few traces of the deposited crystals.

b. Coarse deposit. Fig. 24. The entire specimen has become granular but the outlines and markings of the deposited crystals are but slightly obliterated. The grain size varies over the surface of the specimen. Where the deposited crystals of iron have been small the grains are small and likewise coarse grains are found where the deposit has been coarse. These large grains are shown in Fig. 24. The grain outlines do not follow the crystal outlines but are independent of the previous structure.

5. Heated at 925° for five minutes and cooled in furnace.

a. Fine deposit. The crysalline structure has become granular and the structure is like that obtained in 4a.

b. Coarse deposit. The crystalline structure has changed slightly. The areas at the roots of the deposited crystals have become fine grained while the coarse areas have apparently been unchanged. The resulting structure closely resembles Fig. 22 of 2b.

6. Heated at 950° for five minutes and quenched.

a. Fine deposit. The entire specimen has become fine grained.

b. Coarse deposit. Though the entire specimen is granular the grains vary in size corresponding to the size of the deposited iron crystals.

7. Heated at 950° for fifteen minutes and quenched.

a. Fine deposit. Entire specimen fine grained.

b. Coarse deposit. The structure is not different from that in 6b.

8. Heated at 1,000° for fifteen minutes and quenched.

a. Fine deposit. Fine grained.

b. Coarse deposit. The coarse grains obtained from the coarse crystals at the lower temperatures are breaking up into finer grains.

9. Heated at 1,150° for five minutes and cooled in furnace.

a. Fine deposit. Fig. 25. A fine grained, well defined structure of normal ferrite results.

b. Coarse deposit. Fig. 26. The entire specimen consists of uniform sized grains which are several times larger than those resulting from the fine deposit in 9a.

10. Heated at 1,150° for fifteen minutes and quenched.

a. Fine deposit. Fig. 27. The fine grains do not have as clearly defined boundaries after etching as when annealed from the same temperature. Specimens quenched from the high temperatures show this tendency.

b. Coarse deposit. A grain structure like that of Fig. 26 is produced.

11. Heated at 1,150° for one hour and cooled in furnace.

a. Fine deposit. Fig. 28. After annealing at this high temperature for an hour the fine grains of Fig. 25 have grown slightly but the growth is slow.

b. Coarse deposit. Fig. 29. The grains of Fig. 26 have grown slightly.

12. In this experiment a piece of a dense deposit was heated to near fusion in a platinum crucible. The specimen remained at this high temperature for about five minutes. The resulting structure is shown in Fig. 30. The grains are small and well defined.

The results of these experiments showed that the crystalline structure of electro-deposited iron changed to the usual grain structure at the A_3 point and that the character of the deposited iron determined the rapidity of the recrystallization and also determined the subsequent grain structure.

The experimental work showed that the deposit composed of fine crystals was readily transformed into grains at 900° with a heating period of less than fifteen minutes, while a deposit composed of coarse crystals which had been heat treated with the same sample showed no signs of change. Even with a heat treatment of two hours duration at this temperature the change in structure had only occurred where the crystals were finest.

The above experiments at 900° also show that the time is an important factor. The fine deposit heated for two hours (Fig. 21) showed an almost uniform fine grain structure, while the deposit heated for fifteen minutes (Fig. 20) showed an early stage of the transformation. The coarse deposit when heated at 900° for fifteen minutes showed no change while that heated for two hours showed only a transformation of the smaller crystals.

In experiment 3a where the coarse crystals were heated for one hour at 910° to 915° the transformation was complete, while in experiments 4b and 5b, where the samples were heated for five minutes at 925°, the transformation was barely complete in the one case and partially complete in the second. The discrepancy in 4b and 5b is probably due to different conditions of heating.

The most striking feature was the influence of the crystal size of the deposited iron upon the resulting grains and the stability of the grain size at various temperatures.

This was first noticed in experiments 1a and 2a. In 1a (Fig.

20), the fine deposit, after heating at 900° for 15 minutes, showed large grains in bands where the crystals had previously been dense. But upon heating for two hours at this temperature the large grains were partly divided into smaller ones though not as fine as when heated at 925°.

In experiments 4b where a coarse deposit was heated at 925° for five minutes a peculiar structure resulted. A small grain structure was obtained in the fine crystal areas but in the coarse crystal areas large grains resulted (Fig. 24). At 950° the same structure resulted but at 1,000° the large grains had apparently decreased and the smaller ones had increased in size.

When the coarse crystal specimen had been heated to 1,150° the grains were uniform throughout the specimen (Fig. 26), but these grains were several times larger than those resulting from a similar heat treatment of a fine deposit (Fig. 25).

From the foregoing experiments it is evident that the ferrite grains resulting from the change from the deposited state are influenced by the deposited crystals. The larger these crystals the slower the change to the granular state and the larger the resulting grains. The large grains resulting from a coarse deposit break down at a temperature well above the A_3 point if the time of heating at that temperature is short. With the coarse deposit used and the temperature maintained at the maximum for five minutes the point of breakdown for the large grains is at about 1,000°. That a lower temperature for a longer time will accomplish the same result is evident from experiment 3a, where the grain size differed but slightly over the entire specimen after heating at 910° to 915° for one hour.

This phenomenon is probably best explained by Stead and Carpenter,[6] in their work on the "Crystallizing Properties of Electro-deposited Iron." In their researches they found that when thin strips of electrolytic iron were cooled through the Ar_3 range at any rate short of actually plunging the specimen a coarse crystallization of the iron took place resulting in grains often several millimeters in diameter. They also found that long heating above the Ac_3 point did not result in coarse grains. Their explanation follows:

[6] Journal of the Iron and Steel Institute, Sept., 1913.

"The refining of the structure caused by prolonged heating in the region of gamma iron can be explained in accordance with well established facts of the genesis and growth of crystals in the following way:—On heating the iron strip which consists of an aggregate of alpha crystals, above Ac_3, a region is entered in which gamma is the stable phase, and provided it is held there sufficiently long, not only the alpha crystals, but their nuclei will be destroyed. When the strip is cooled through Ar_3, and again enters the alpha region, it is, *a priori,* a question whether a large number of alpha nuclei will be formed simultaneously, in which case the crystals that result from them will be both numerous and small, or a small number of nuclei are formed, in which case, provided diffusion can take place with sufficient rapidity, the nuclei will develop into a small number of large crystals, or, of course, any intermediate proportion may be assumed. A reasonable explanation of the fine alpha crystallization resulting from prolonged heating in the gamma region is, therefore, that very numerous alpha nuclei are formed simultaneously on passing through Ar_3, and accordingly the crystals are small. On the other hand, a short heating above Ac_3 may be insufficient completely to destroy the alpha nuclei, and when the strip cools through Ar_3 a certain number will be present which will act as centers of crystallization, so that, if diffusion is operative, large crystals will grow from these centers. This would account for the coarse crystallization that results after a short heating above Ac_3, and it is the explanation which appears to the authors to be reasonable, and to fit in with the observed facts."

In the author's work the electrolytic iron was used in thick sections of from ten to twenty grams in weight instead of strips 0.01 inch or less in thickness. The coarse crystallization obtained is not to be compared with that obtained by Stead and Carpenter though the general nature of the phenomena is the same. Though the specimens were quenched, the rate of cooling was probably slow, due to their weight. The persistence of the large crystals and the formation of the large grains is explained by the persistence of the alpha or non-gamma crystals.

Stead and Carpenter,[7] in their work, showed that the iron used

[7] Journal of the Iron and Steel Institute, Sept., 1913.

did not coarsen perceptibly upon heating beyond Ar_3. Howe[8] states that he was able to coarsen electrolytic iron somewhat upon heating to 1,300°. These experiments also show that electrolytic iron when heated in the gamma range does not coarsen appreciably at temperatures up to 1,150°.

SUMMARY.

1. No change in structure of electrolytic iron could be determined at temperatures below the A_3 range.

2. A fine deposit is more readily changed to the grain structure than a coarse deposit.

3. With a short heating above the A_3 range the fine deposit is transformed into a fine grain structure while a coarse deposit becomes coarse grained.

4. The coarse grains resulting from a coarse deposit may be broken down into smaller grains by long annealing at the Ac_3 point or by heating to 1,000° or higher.

5. The grain structure resulting from a fine structure is always finer than that resulting from a coarse deposit.

6. The grains of electrolytic iron do not grow appreciably at 1,150°.

MICROSTRUCTURE OF FUSED ELECTROLYTIC IRON.

Three samples of fused electrolytic iron were used in this study, all samples being in the form of small ingots made in a vacuum furnace. Ingot A was obtained through the courtesy of Mr. Arsem, of Schenectady, New York. Ingot B was made by Dr. O. P. Watts, and ingot C by Mr. L. T. Richardson, at the Chemical Engineering Laboratories of the University of Wisconsin. These ingots were halved, polished, and etched and are shown in Figs. 31, 32 and 33.

Fig. 31 shows ingot A. The heat treatment of this sample is not known. By comparison with ingots B and C, whose history is known, it probably was kept in the fused state for a long period and then allowed to cool slowly. The sample shows a coarse grain, as seen in Fig. 31. Some of the grains are from 5 to 7 mm. in diameter. The ingot shows a small pipe and numerous blow

[8] Bulletin Am. Inst. Min. Eng. No. 84, p. 2821.

holes. It is evident that these blow holes were filled by a reducing gas, probably hydrogen, since the iron surrounding them was bright and untarnished.

Fig. 32 shows ingot B, which was melted in a magnesia crucible. Upon heating the electrolytic iron to above its melting point a violent evolution of gas took place. After two hours of heating at about 1,600° to 1,700° the gas continued to come off at a slow rate. The ingot was then cooled in the furnace, the cooling from the melting temperature to a low red occupying about 15 minutes. The large pipe with the absence of blow holes and the small grains are the striking features of this ingot.

Fig. 33 shows ingot C. The iron was heated to about 1,600° when a violent evolution of gas took place. After ten minutes the ingot was allowed to cool Upon the first freezing of the outside portions of this ingot the interior began to boil, throwing small particles of iron above the surface of the ingot. The result of this violent evolution of gas is evident in the photograph. Not only has a large pipe and cavity with numerous blow holes resulted, but a collar of metal has been formed about the top of the ingot by the ejected metal. The grain size is the same as that of ingot B.

Fig. 34 shows the surface of ingot A after etching with picric acid. The grain is coarse and several grains are apparently merging into each other as is seen by the disappearing boundary lines of some of the grains. A large blow hole is seen in one corner and smaller pits are distinguishable upon the surface.

Fig. 35 is a micrograph of the structure near the surface of the ingot, showing the orientation of the ferrite grains at right angles to it. Here again grain boundaries are disappearing to form larger grains.

The etching of this specimen was continued, by alternating the picric acid with a four percent solution of nitric acid in amyl alcohol. This etching was continued for over two hours and developed the structures shown in Figs. 36 to 40. These micrographs not only show the coarse grains developed with the first etching, but also show the devolopment of a new structure in the interior of these grains. These sub-grains will be called "inner grains" for convenience.

Each grain showed an inner grain structure, though some had developed this structure only slightly. The size of the inner grains varied in different grains.

Fig. 36 shows several grains of ferrite. The inner grains are of the same size in neighboring grains, though varying in the same one. The attack of the etching reagent is more noticeable in the darker grains and the inner grain boundaries are more prominent.

In Fig. 37 the attack has been heavier, and, although the light area does not show an inner grain structure in the micrograph, a close examination of the specimen showed that this structure was present.

A study of the boundaries of the grains and the inner grains showed a marked difference in their appearance. While the boundaries of the grains seemed to be "V" shaped grooves those of the inner grains were merely shallow depressions. Upon etching for a prolonged period the inner grain structure of Figs. 38, 39 and 40 was developed. The shallow troughs were deepened by this prolonged etching until a series of pits developed. The deepening of the inner grain boundaries by these pits is shown in the partly developed inner grains of Figs. 38 and 39.

Two neighboring grains having a differing crystal orientation did not show any continuity of inner grain structure. The boundary between these two grains did not allow any continuance of inner grain boundaries. But in the neighboring grains where the crystal orientation was similar, the inner grains were often continuous. This was especially true with boundary lines which were partly obliterated. In these cases the crystal orientations were similar and the boundary lines were slowly disappearing. A large number of these vanishing boundary lines were present in the specimen. Deep etching developed pits along these vanishing boundary lines while the "V" shaped grooves pitted but slightly. Some of the larger inner grains, when examined under higher magnifications, seemed to be subdivided into two or three smaller grains by shallow trenches which were barely noticeable.

Upon annealing a specimen of this iron at 925° the large grains were partly broken down and the inner grain structure persisted, but not as marked as in the original specimen. Upon

annealing at 950° and then at 1,150° the large grains were completely broken down and only traces of the inner grains remained.

The inner grain structure surrounding a blow hole was much finer than the normal size. This is shown in Fig. 40.

The significant facts in connection with this inner grain structure follow:

1. Each ferrite grain has a peculiar inner grain size.

2. The inner grain boundaries are shallow depressions.

3. The development of the inner grain depends upon the crystal orientation of the grain.

4. The boundaries of the grains are more quickly developed than the inner grain boundaries.

5. Two adjacent grains of dissimilar crystal orientation show no continuity through their boundaries of the inner grain boundaries.

6. Two merging grains show a continuity through their boundaries of the inner grain boundaries.

7. Deep etching causes the shallow depressions to become pitted.

8. Several annealings above the Ac_3 point were required to destroy the inner grain structure.

From these observations the following explanation of this peculiar structure is offered. The inner grains are probably groups of similarly oriented iron crystals. The orientation in all of these groups is alike throughout the ferrite grain. In slowly cooling from the molten state large gamma grains are formed. In changing from the gamma state to the non-gamma state the grain size remains the same. Stead and Carpenter's[10] explanation previously quoted states that a fine grain structure is due to a large number of non-gamma nuclei.

If we consider that, owing to the large gamma grains, a large number of non-gamma nuclei were formed in each gamma grain and that each nucleus was similarly oriented owing to similarly oriented gamma crystals, we can readily see that the ferrite grains would be composed of a large number of groups of similarly oriented crystals.

These groups of crystals would constitute the inner grains. Each nucleus would grow until it met a neighboring group. In

[10] Journal of the Iron and Steel Institute, Sept., 1913.

this case the crystals would be similarly oriented in the neighboring groups and the boundaries would consist of more or less imperfect and smaller crystals, but of like orientation. In etching, this boundary would etch more rapidly and would cause a depression to be formed resulting in the inner grain boundaries. That the boundaries consist of crystals whose orientation is the same as those of the inner grains is probably correct, since the rate of etching of the boundary is proportional to the rate of etching of the entire grain surface. That is, those grains coloring quickly when etched, owing to their crystal orientation, show the inner grain structure first. This is shown in Figs. 36 and 37.

Humfrey,[11] in his work on "The Intercrystalline Fracture of Iron and Steel," developed a somewhat similar structure by heating a polished strip of Swedish Iron in a vacuum furnace. The etching reagent was CO_2, a slight amount of which was given off by the Mabor slabs supporting the specimen. The section of the specimen heated to the Ar_2 to Ar_3 region showed ferrite grains, some of which showed an inner network of fine lines. The section heated to between the Ar_1 to Ar_2 limits showed iron grains with a network of etching figures closely resembling the inner grains. The boundaries of the grains were also "V" shaped grooves, as were those obtained by the author in his work. The similarity between the two is striking, although the author worked with grains many times larger than those of Mr. Humfrey.

Upon annealing a section of Ingot A, at 950° for one hour, the structure shown in Fig. 41 was obtained. Areas of fine grains intermingled with larger grains resulted. Upon annealing at 1,150° for three hours larger grains were again formed. The boundaries of these grains after this heat treatment again showed a tendency to be discontinuous as in the original specimen. Deep etching showed a few traces of the original inner grain structure.

The microstructure of Ingot B is shown in Fig. 42. The grains are small and the iron appears unclean, small dots appearing over the surface, probably due to remaining gases. A large number of these fine inclusions appear in the grain boundaries. The grains are also covered with a network of fine lines.

Upon annealing Ingot B at 950° for one-half hour the normal

[11] Carnegie Scholarship Memoirs, IV, p. 80.

ferrite structure of Fig. 43 was obtained. The fine network still appears in the ferrite grains while the inclusions seem to have almost disappeared with the exception of few spots. When annealed at 1,050° for 15 minutes the structure of Fig. 44 was obtained. The ferrite grains of Fig. 43 have grown. The network is still visible while few inclusions remain. When annealed at 1,150° for three hours the structure, shown in Fig. 45, resembles the original structure (Fig. 42). The grains are slightly coarser but the inclusions are segregated in the grain boundaries. A fine network covers the grains.

The structure of Ingot C did not differ materially from that of Ingot B (Fig. 42). The amount of inclusions was greatly increased. The grain size was the same and a network of fine lines in the grains was also present.

ROLLED ELECTROLYTIC IRON.

Several cathodes of electrolytic iron were heated and rolled into standard gauge sheets. A microscopic examination showed a structure of clean ferrite. (Fig. 46).

FORGED ELECTROLYTIC IRON.

In the investigation of the properties of iron alloys electrolytic iron was used as a source of pure iron. In this work rods of pure forged electrolytic iron served as a standard for comparison. The iron was melted in a magnesia crucible in a carbon resistor furnace. The ingot obtained was forged into a rod of the desired size. The microstructure of such a forged rod is shown in Fig. 47. The structure consists of fine grained ferrite with a minimum of impurities.

Under some conditions of melting carbon was absorbed from the CO atmosphere in the crucible and a low carbon steel resulted. A microsection of a forged rod containing a small percentage of absorbed carbon is shown in Fig. 48.

Chemical Engineering Laboratories,
University of Wisconsin.

UNIVERSITY OF ILLINOIS LIBRARY

FIG. 1. × 3

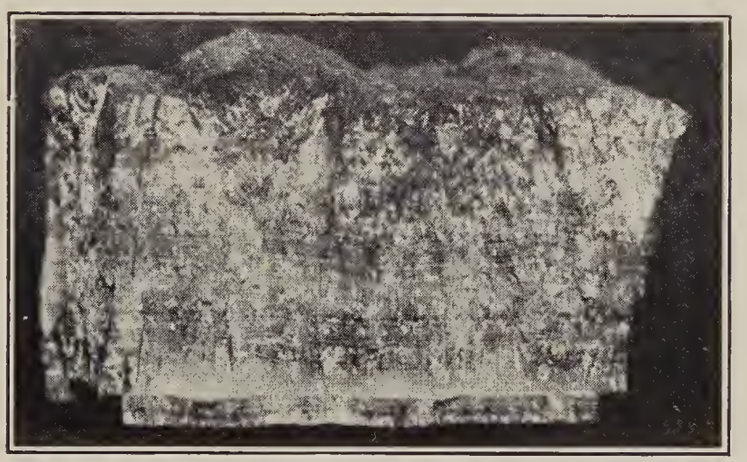


FIG. 2. × 3

FIG. 3. × 4

FIG. 4. × 1½

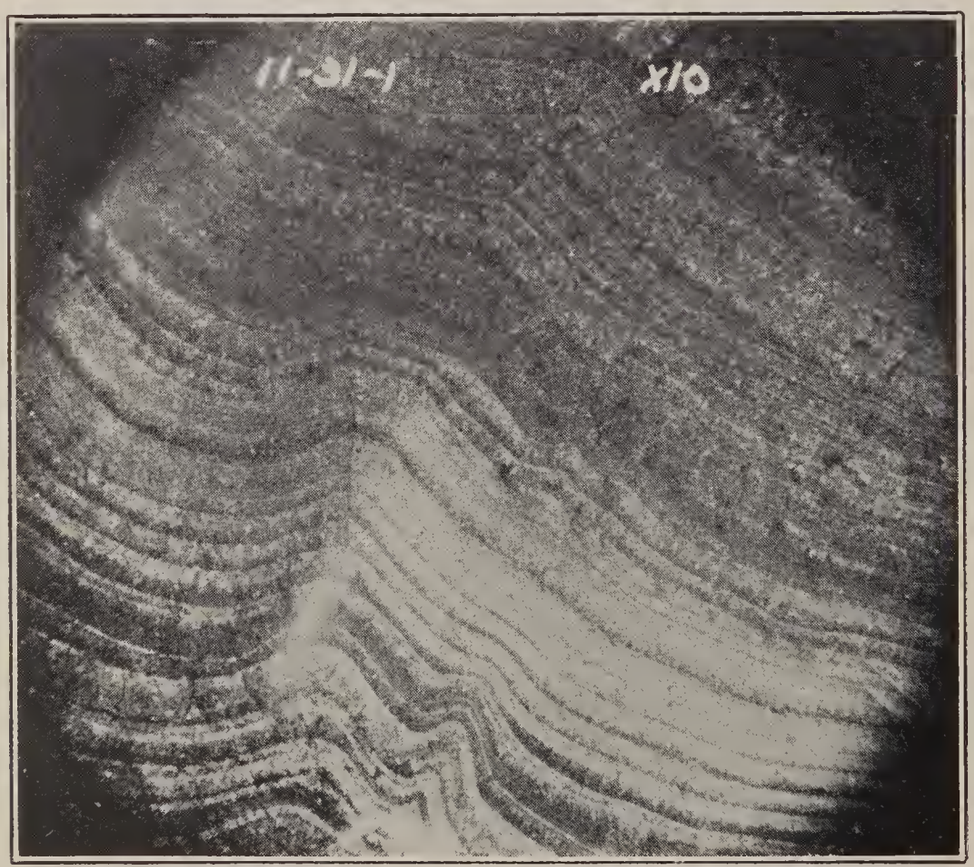


FIG. 5. × 10

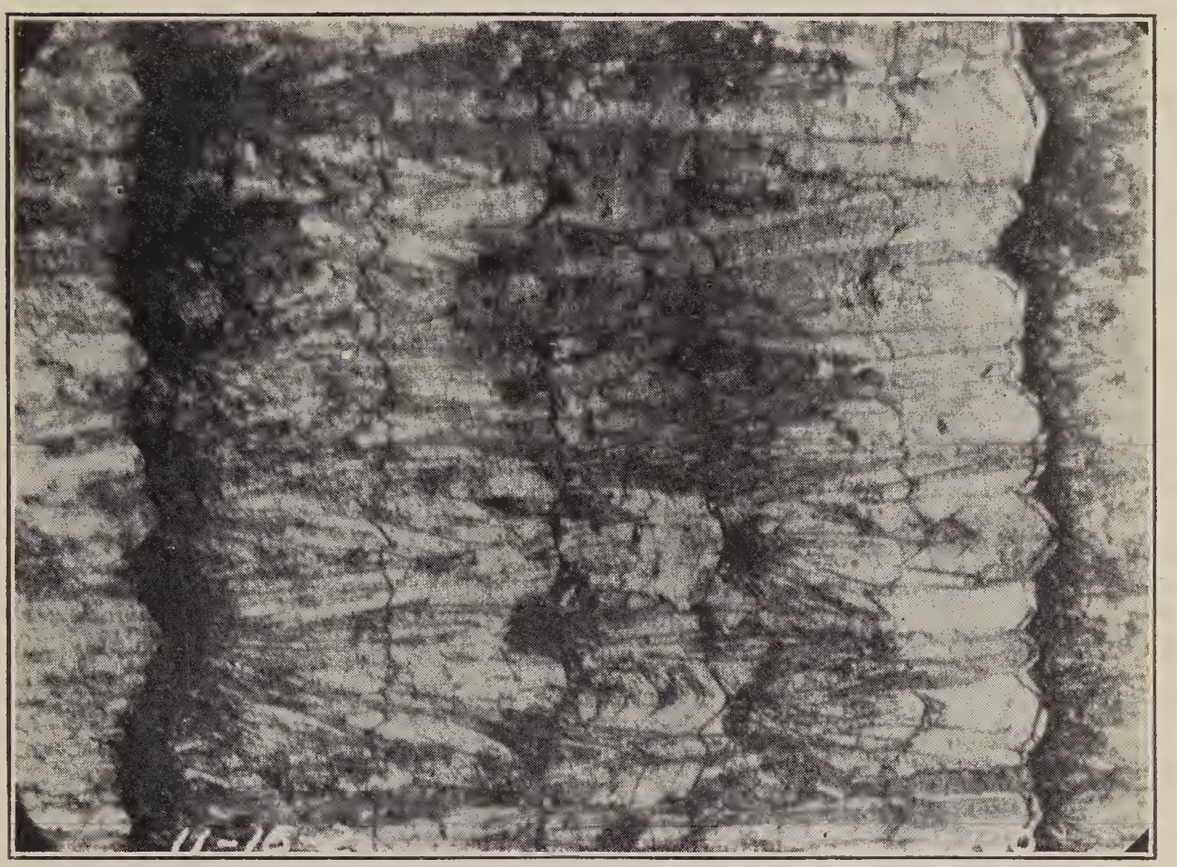


FIG. 6. × 100

FIG. 7. × 100

FIG. 8. × 100

FIG. 9. × 300

FIG. 10. × 100

FIG. 11. × 100

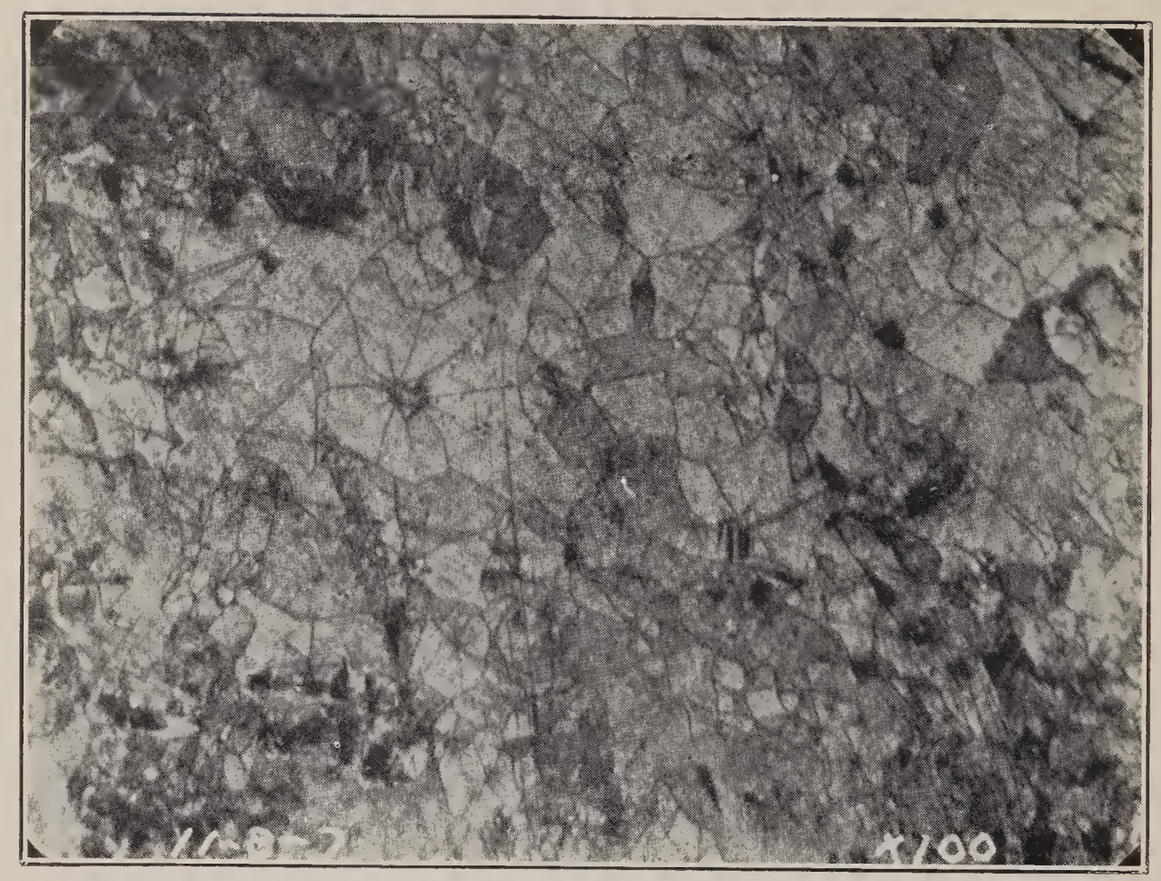


FIG. 12. × 100

FIG. 13. × 100

FIG. 14. × 70

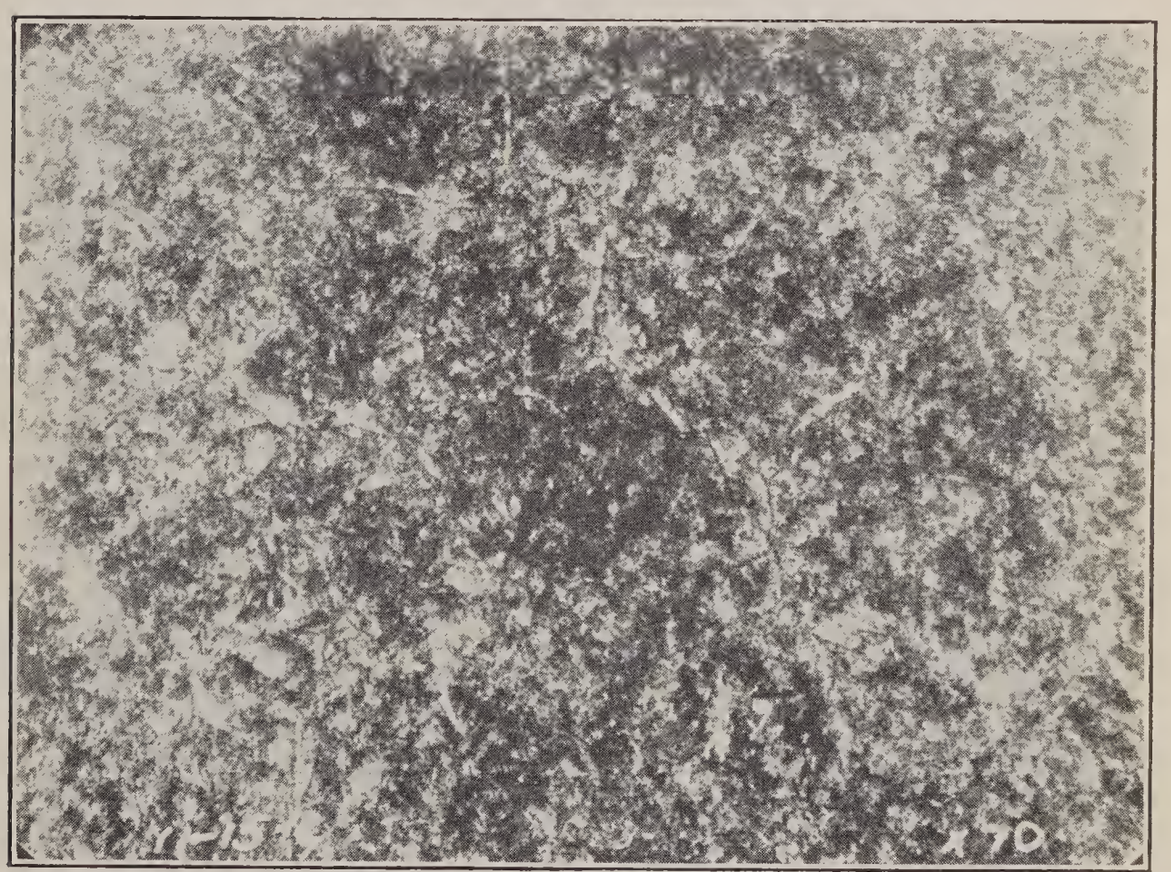


FIG. 15. × 70

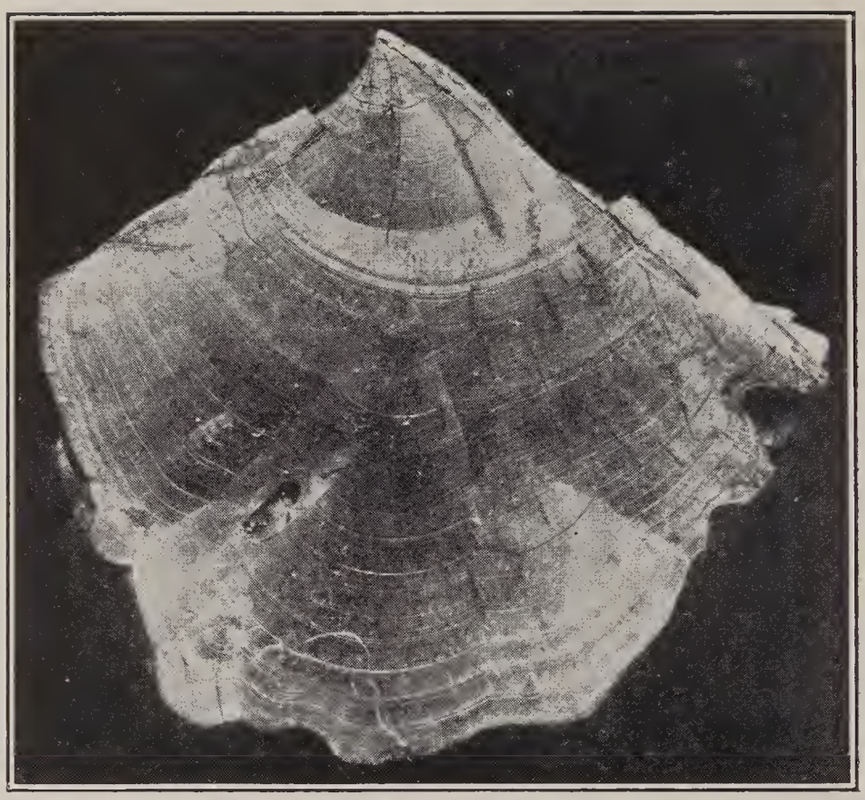


FIG. 16. × 4

FIG. 17. × 25

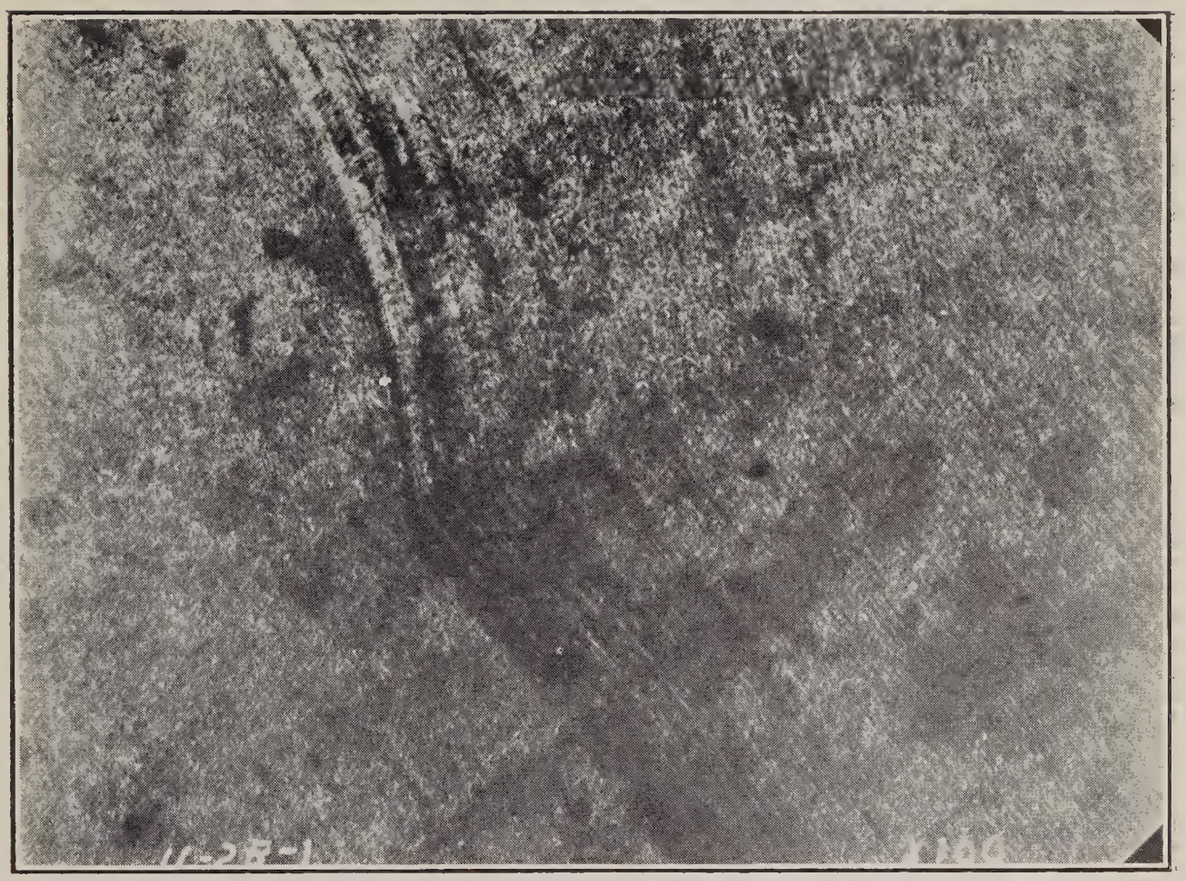


FIG. 18. × 100

FIG. 19. × 100

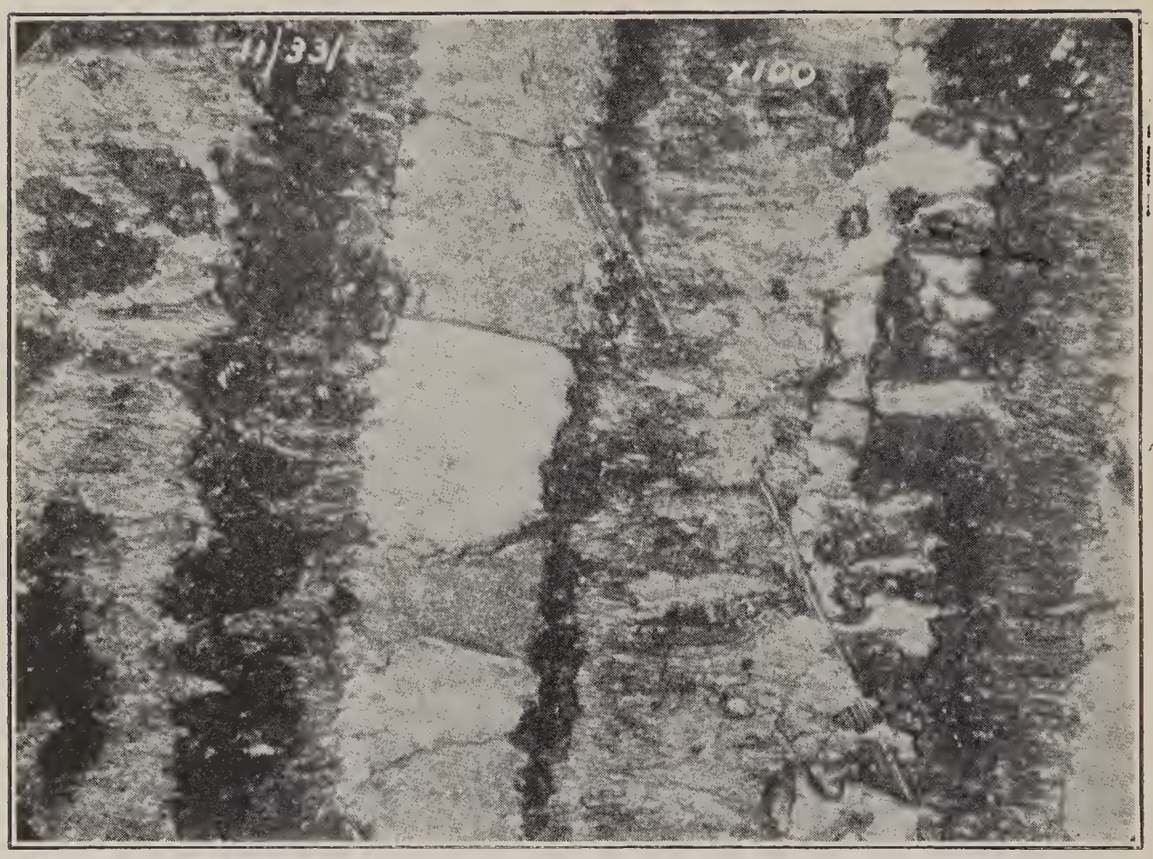


FIG. 20. × 100

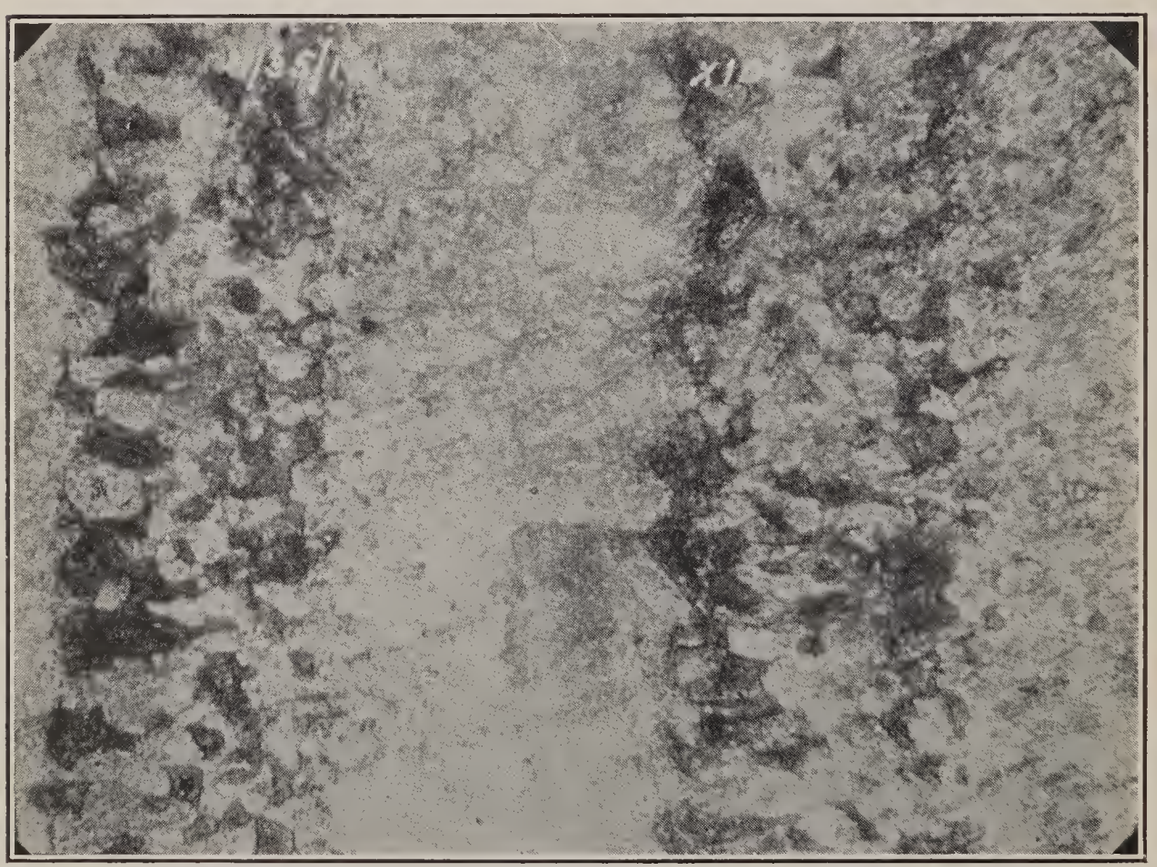


FIG. 21. × 100

FIG. 22. × 100

FIG. 23. × 100

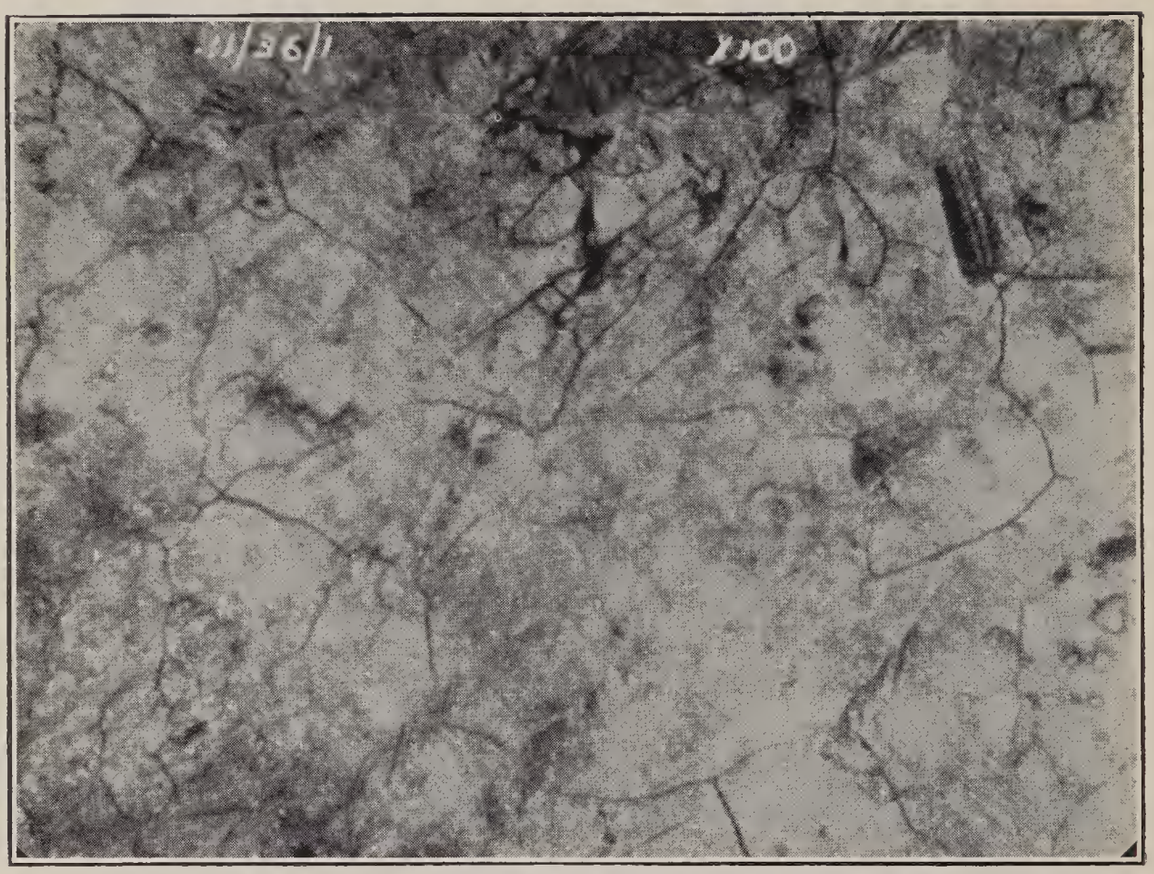


FIG. 24. × 100

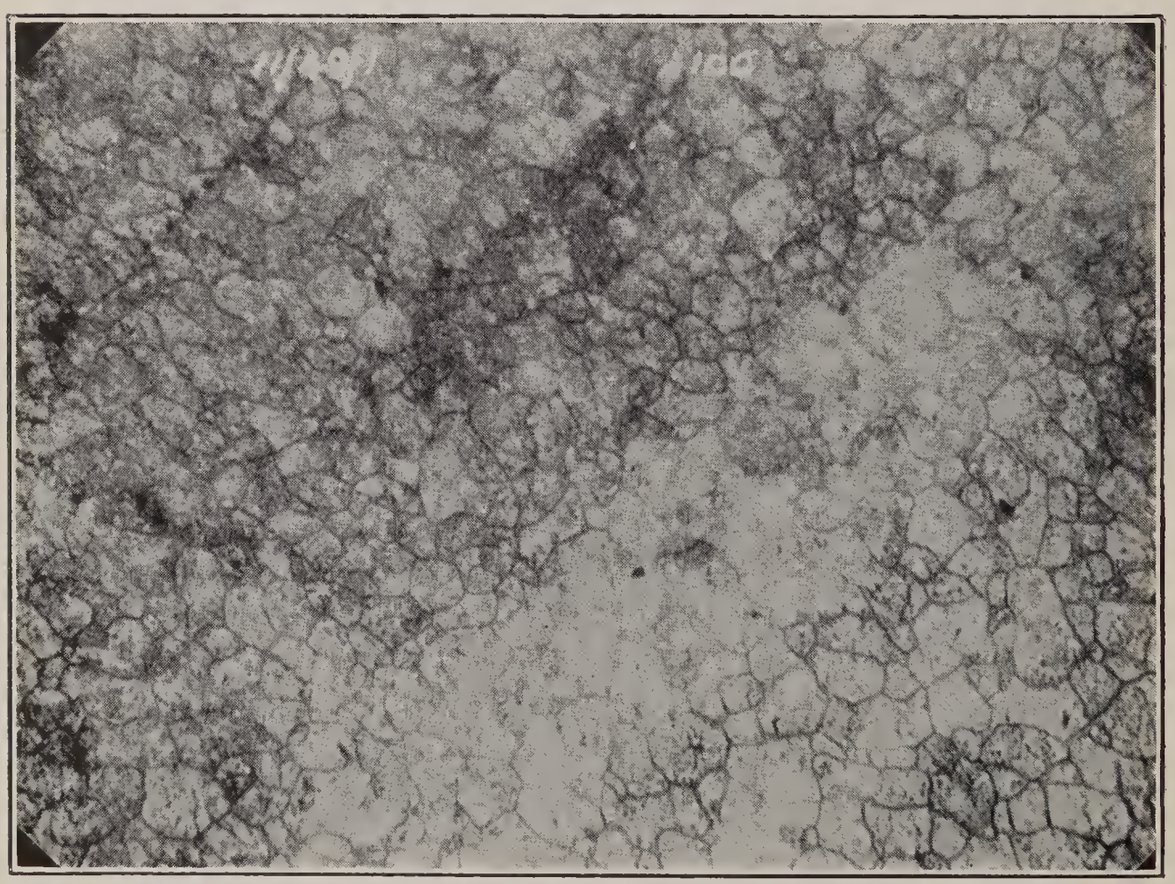


FIG. 25. × 100

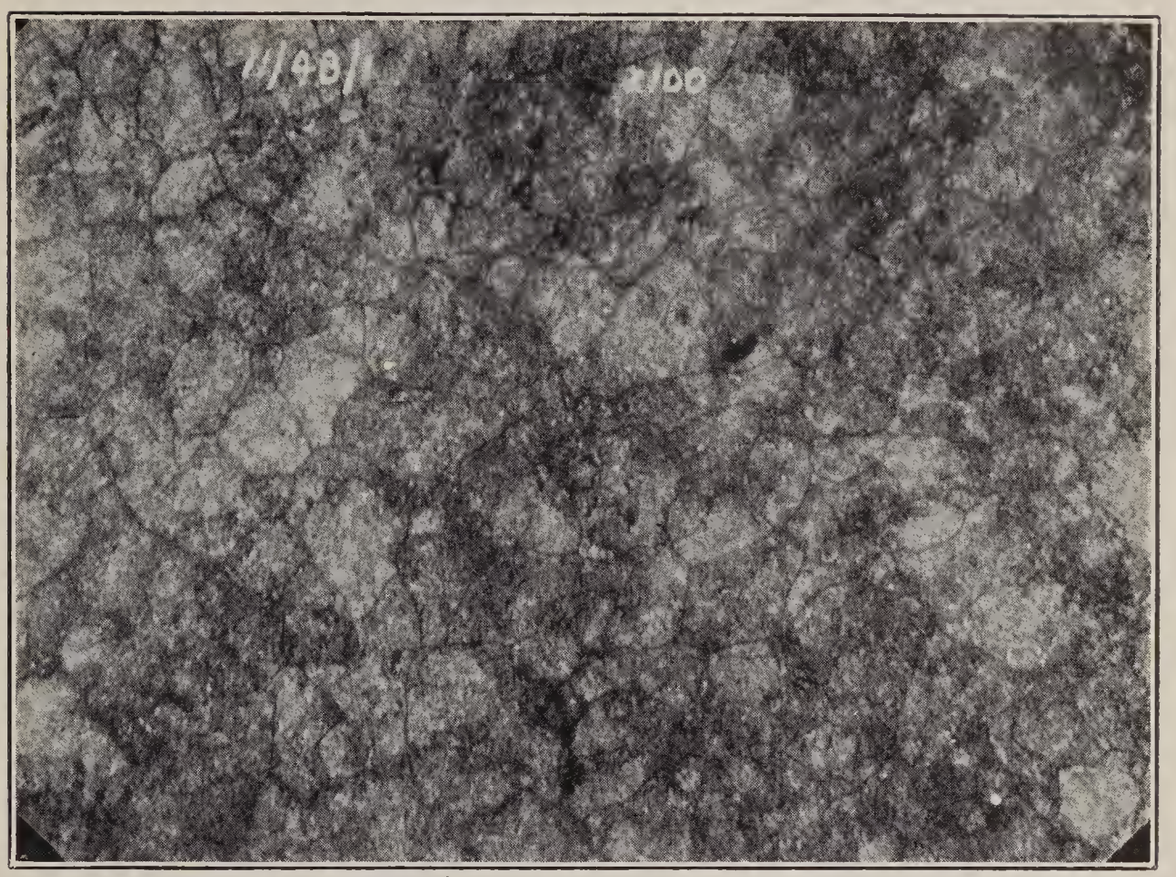


FIG. 26. × 100

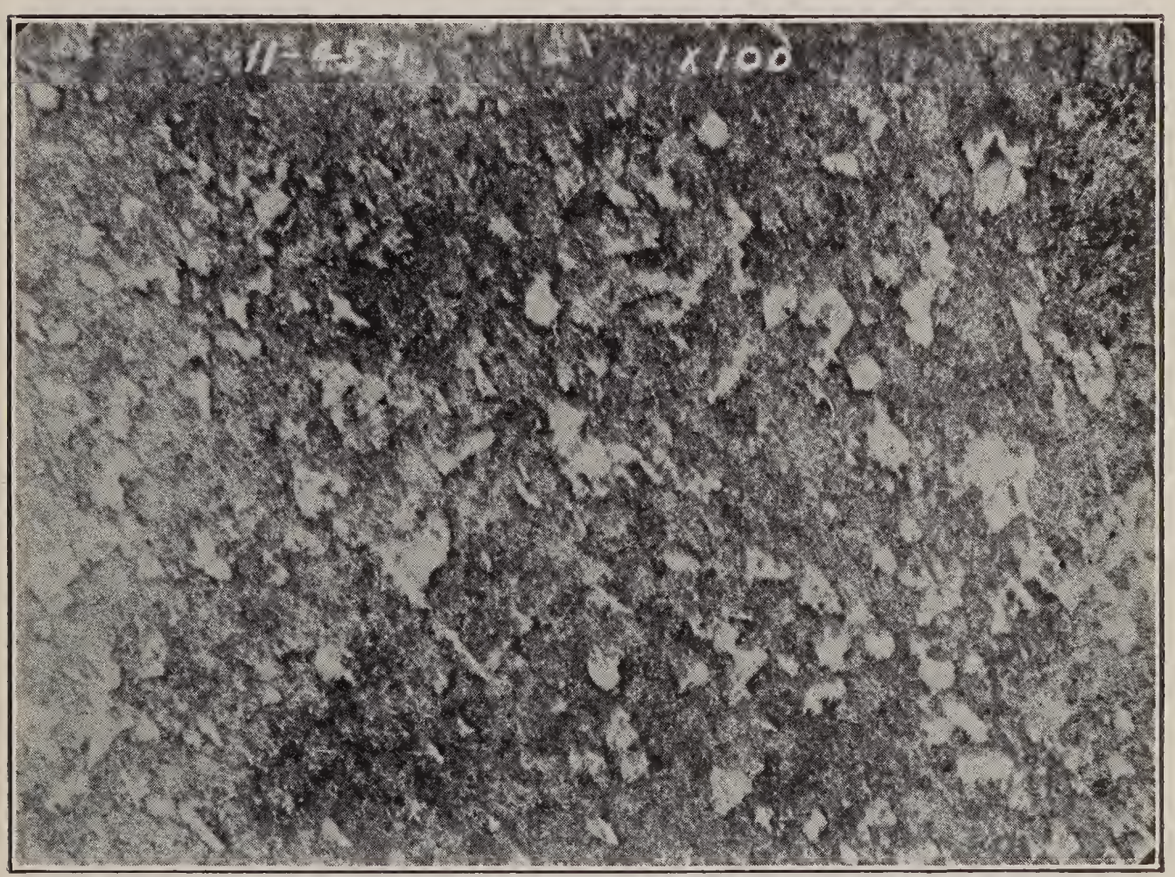


FIG. 27. × 100

FIG. 28. × 100

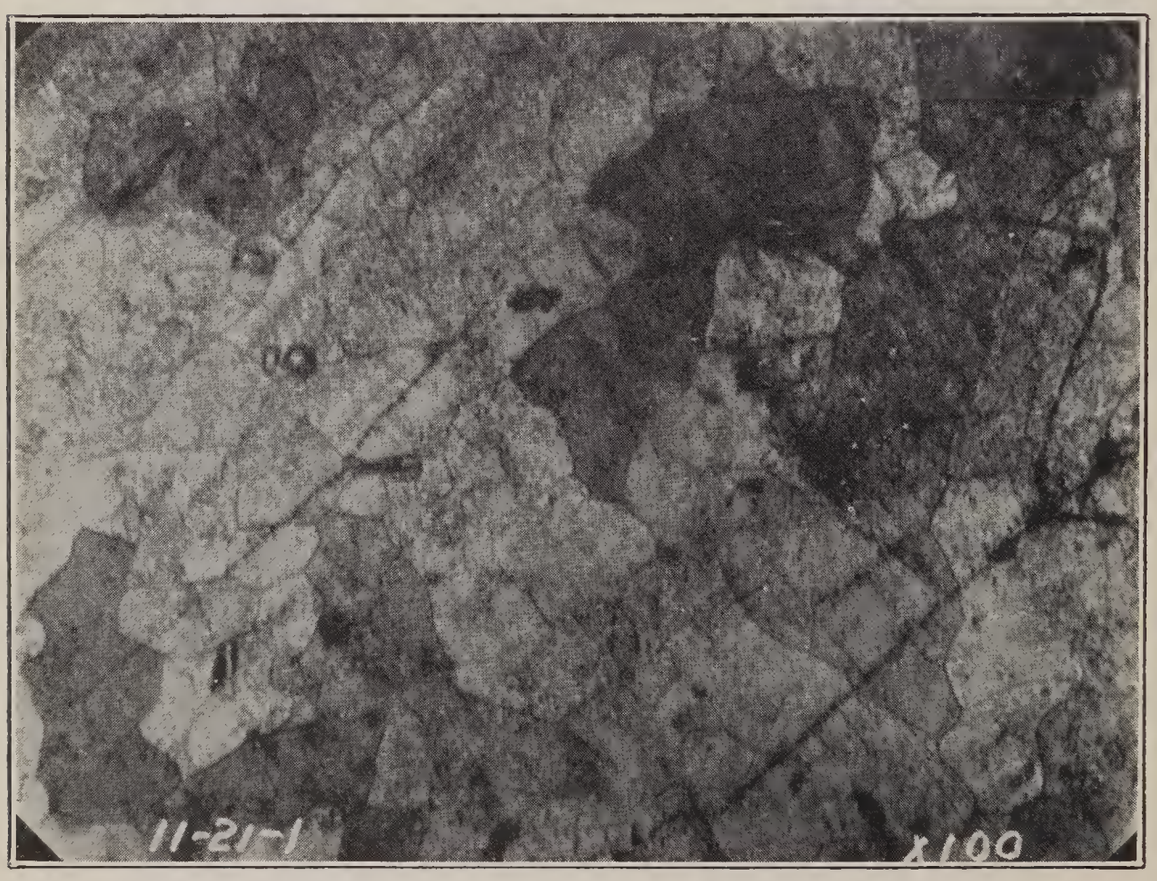


FIG. 29. × 100

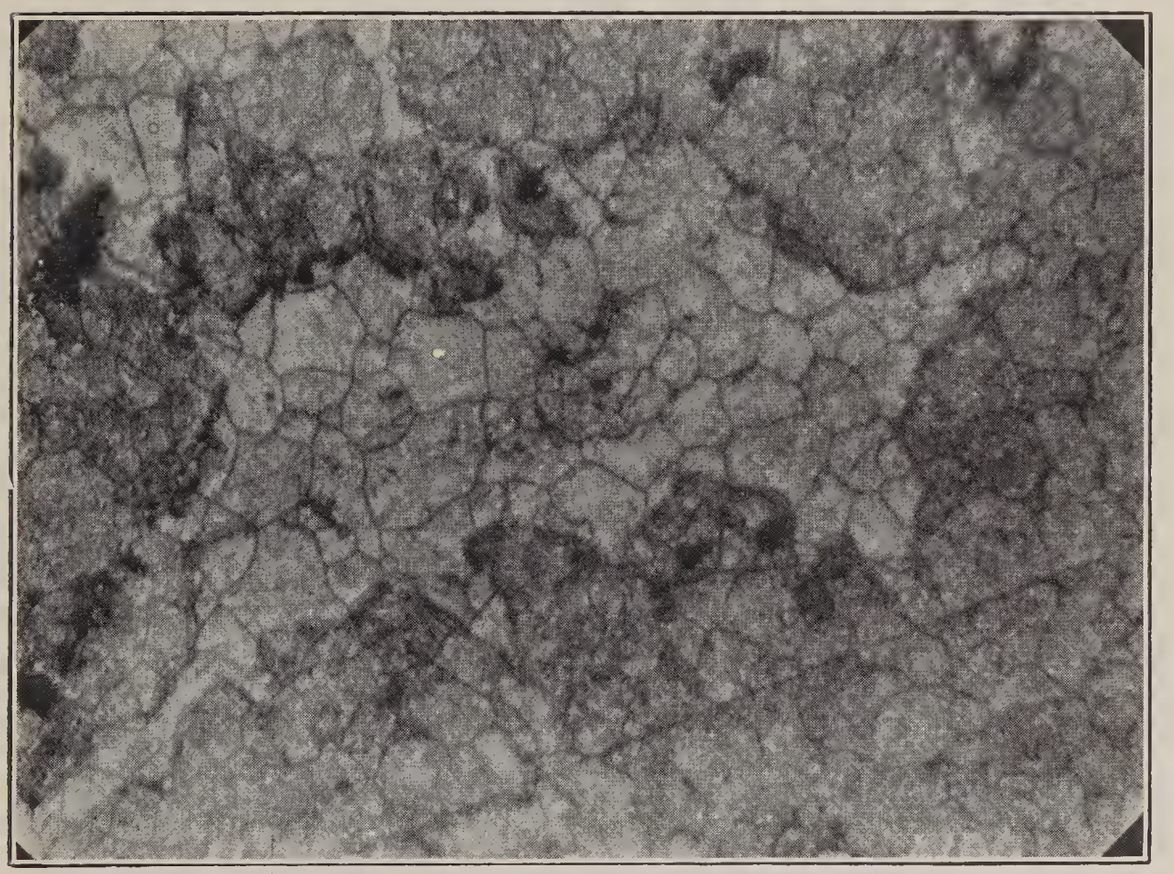


FIG. 30. × 100

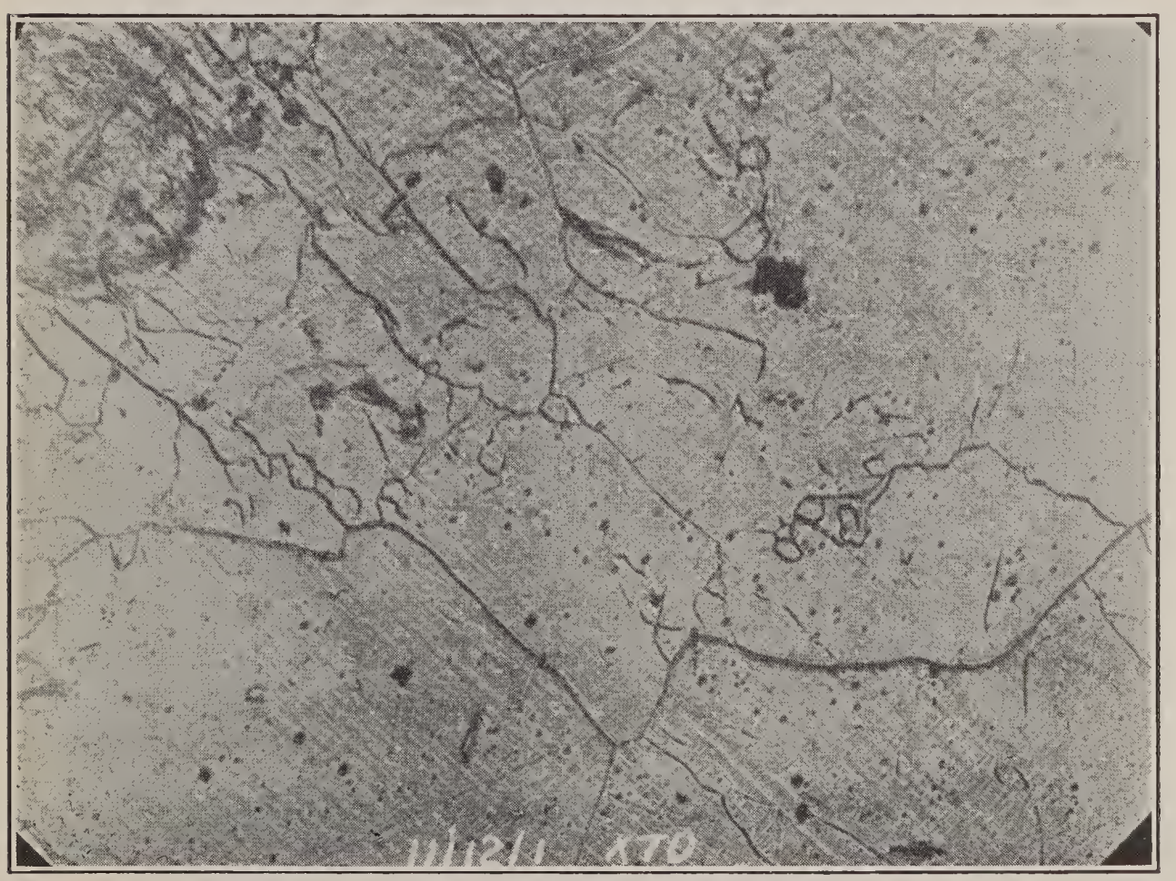


FIG. 34. × 70

FIG. 31. × 2

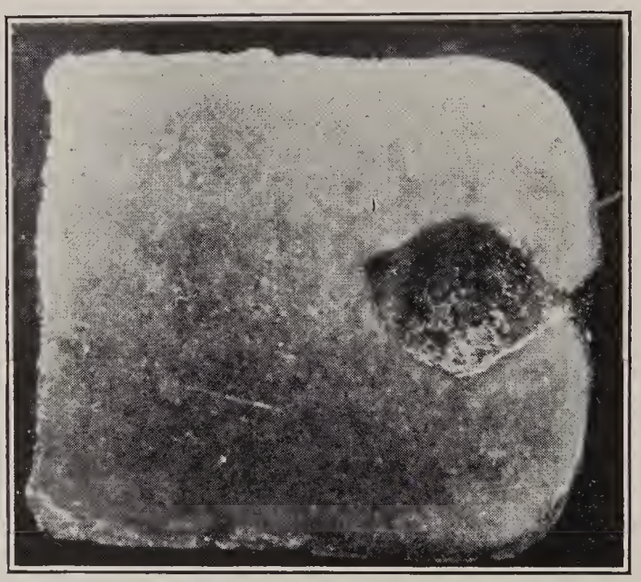


FIG. 32. × 2

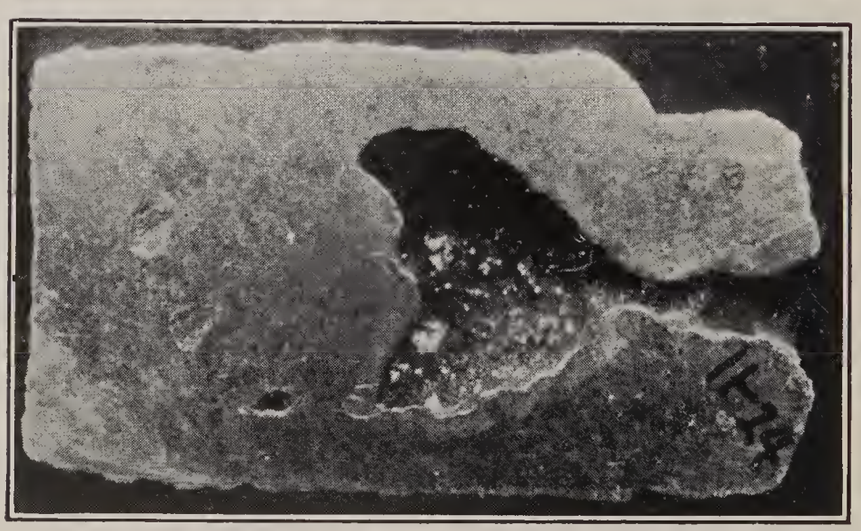


FIG. 33. × 2

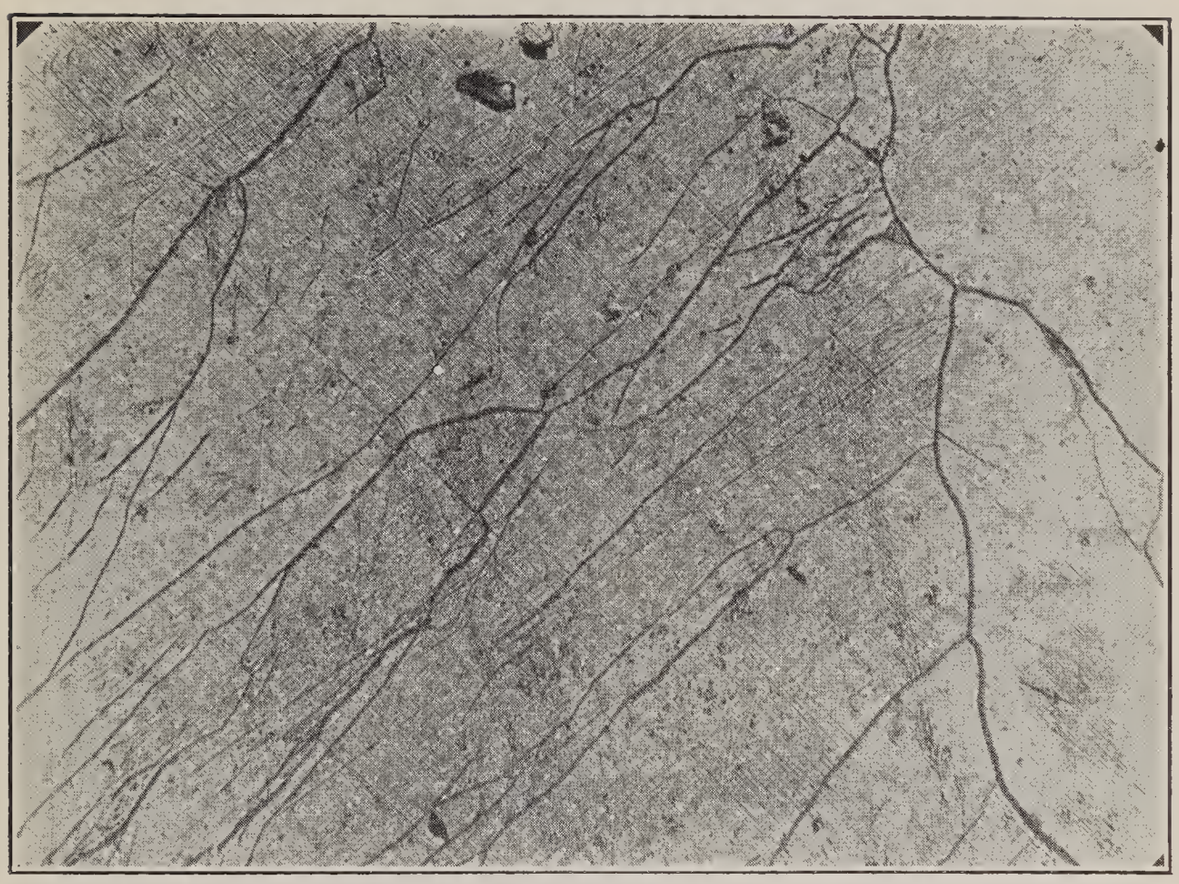


FIG. 35. × 70

FIG. 36. × 70

FIG. 37. × 70

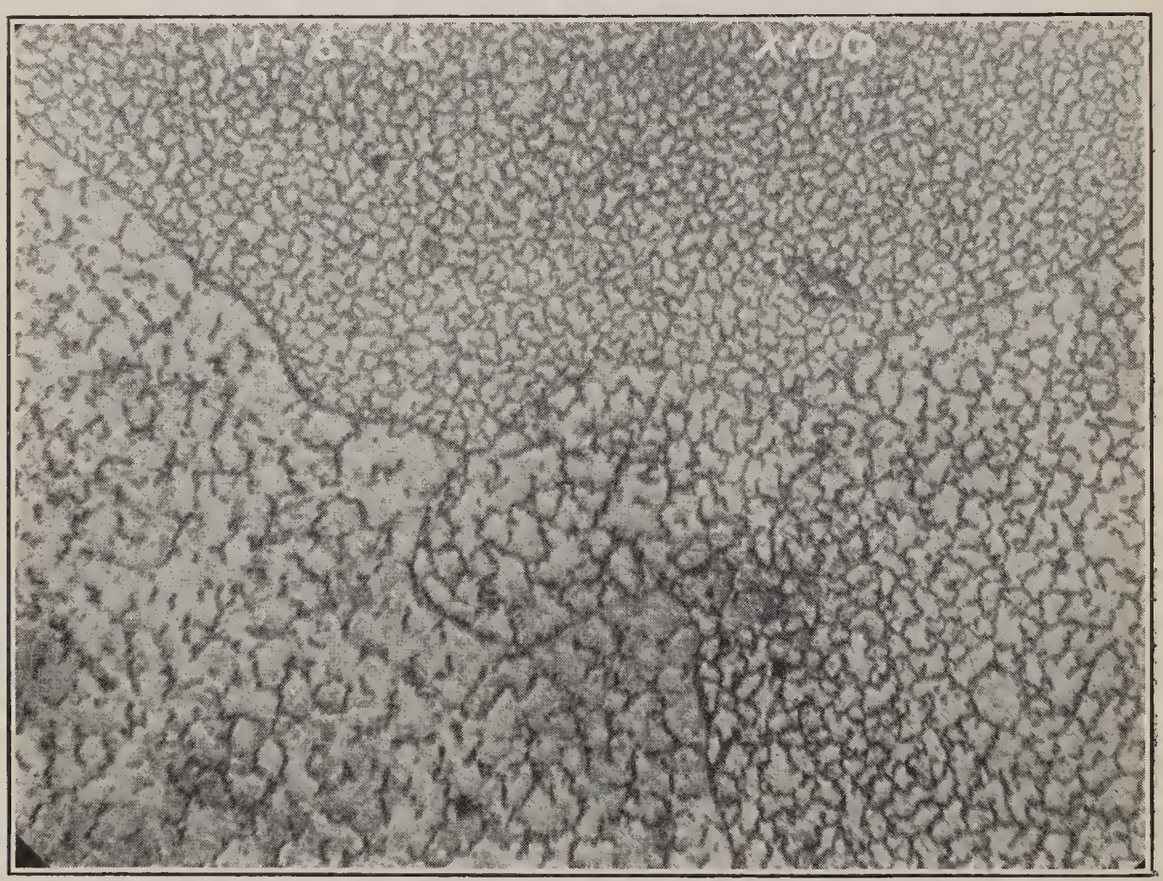


FIG. 38. × 100.

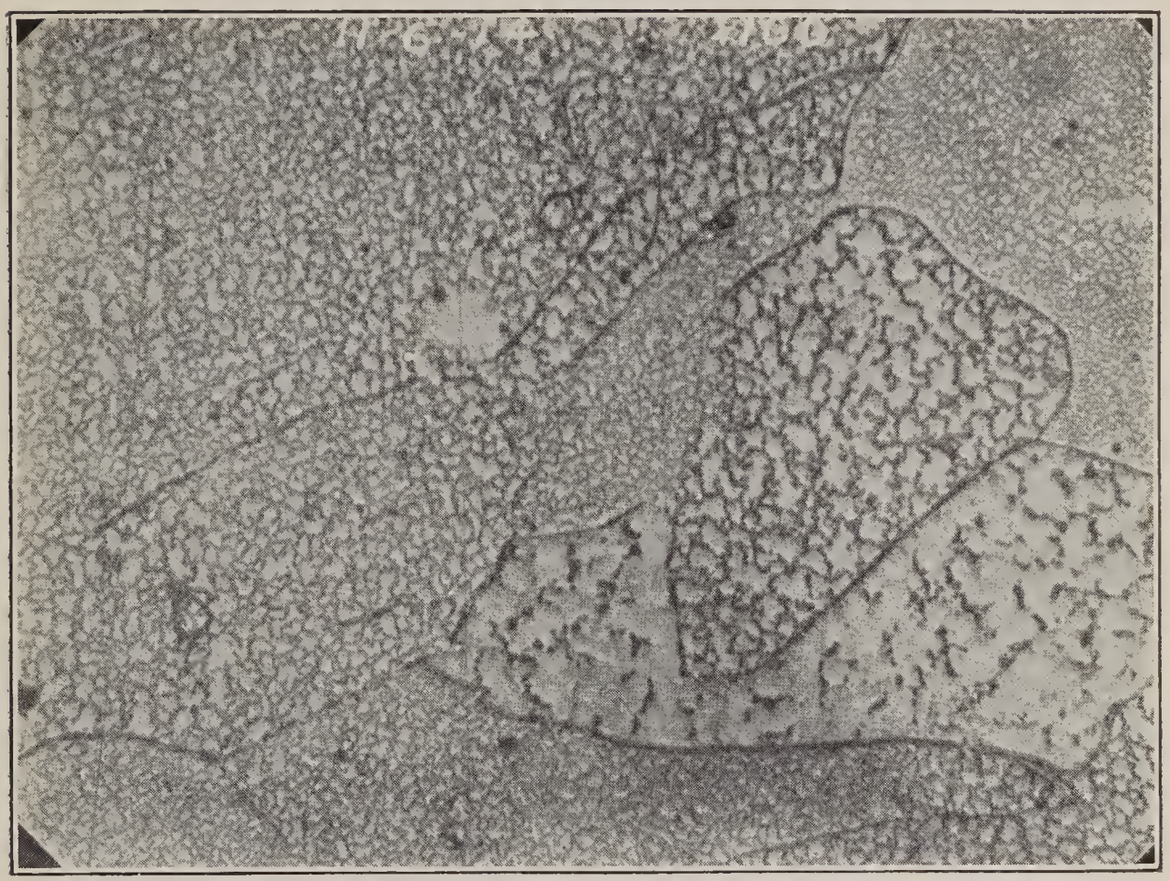


FIG. 39. × 100

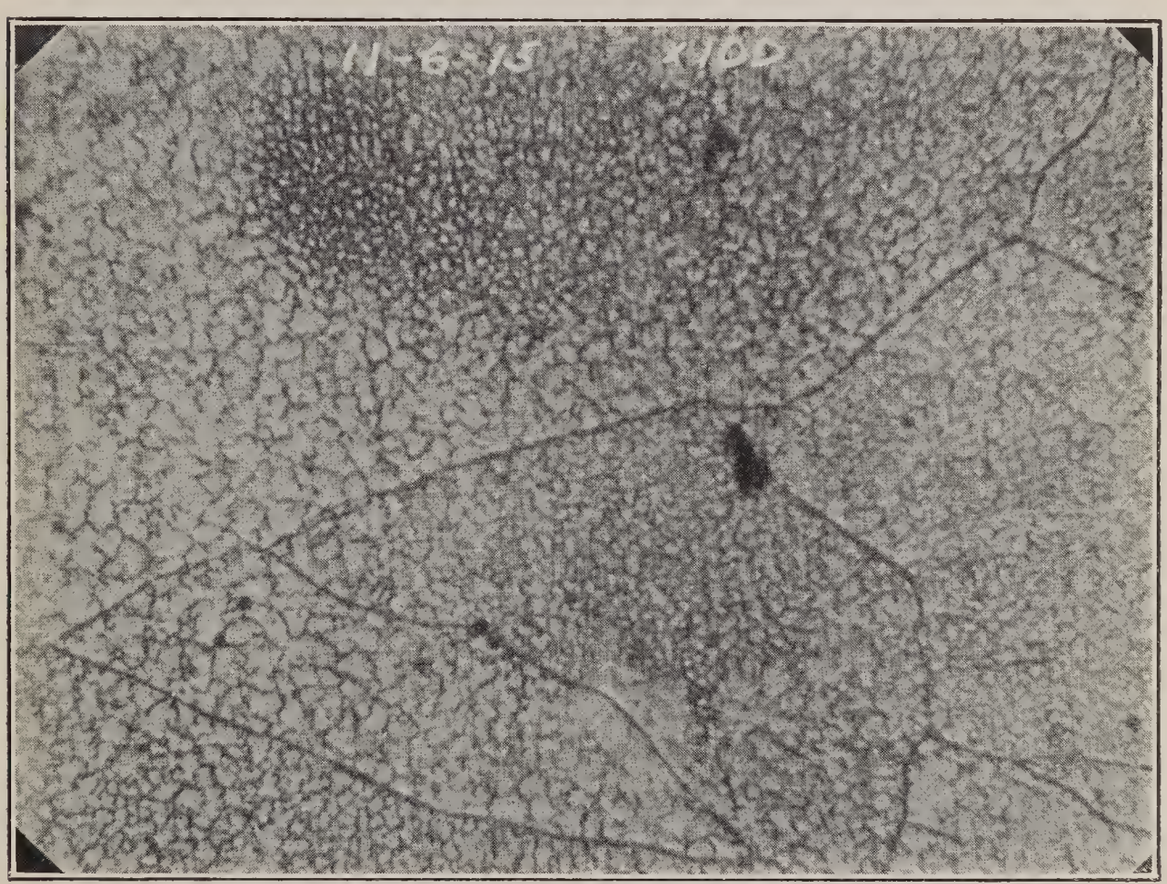


FIG. 40. × 100

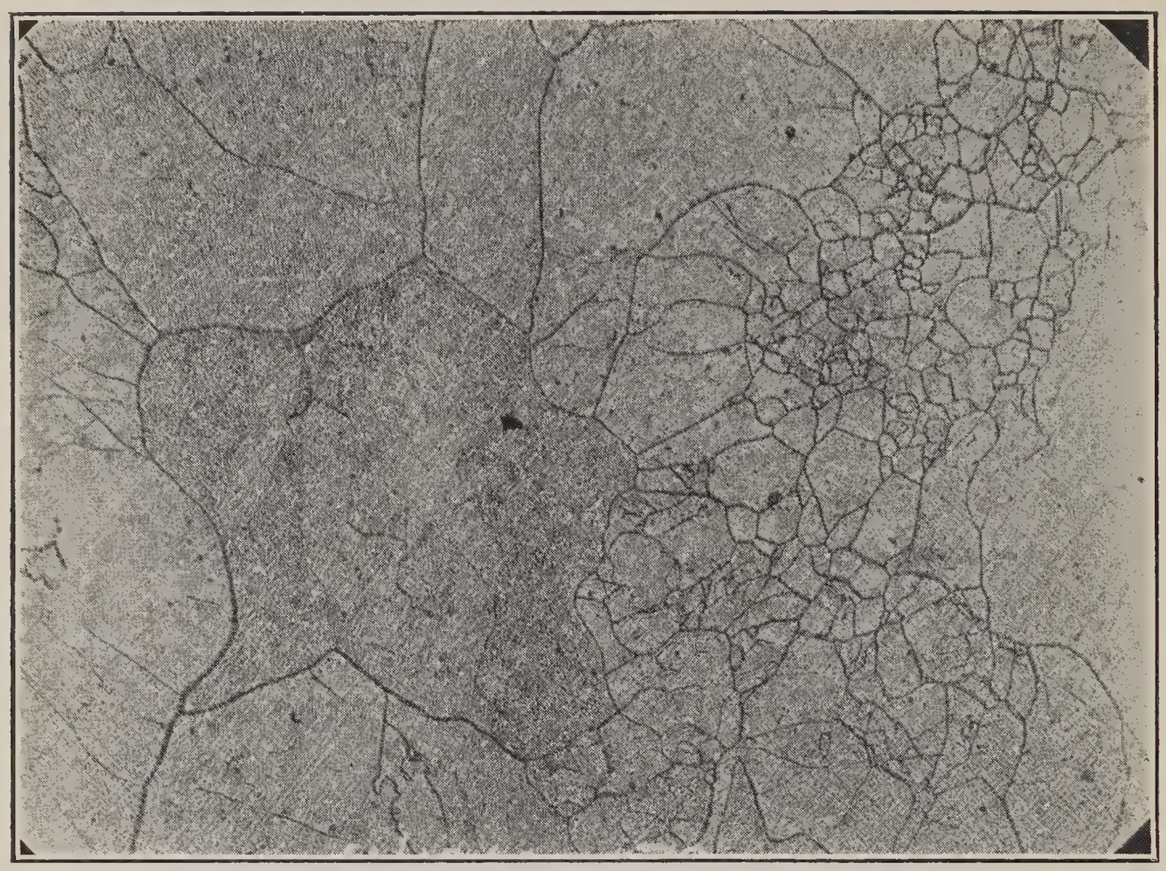


FIG. 41. × 70

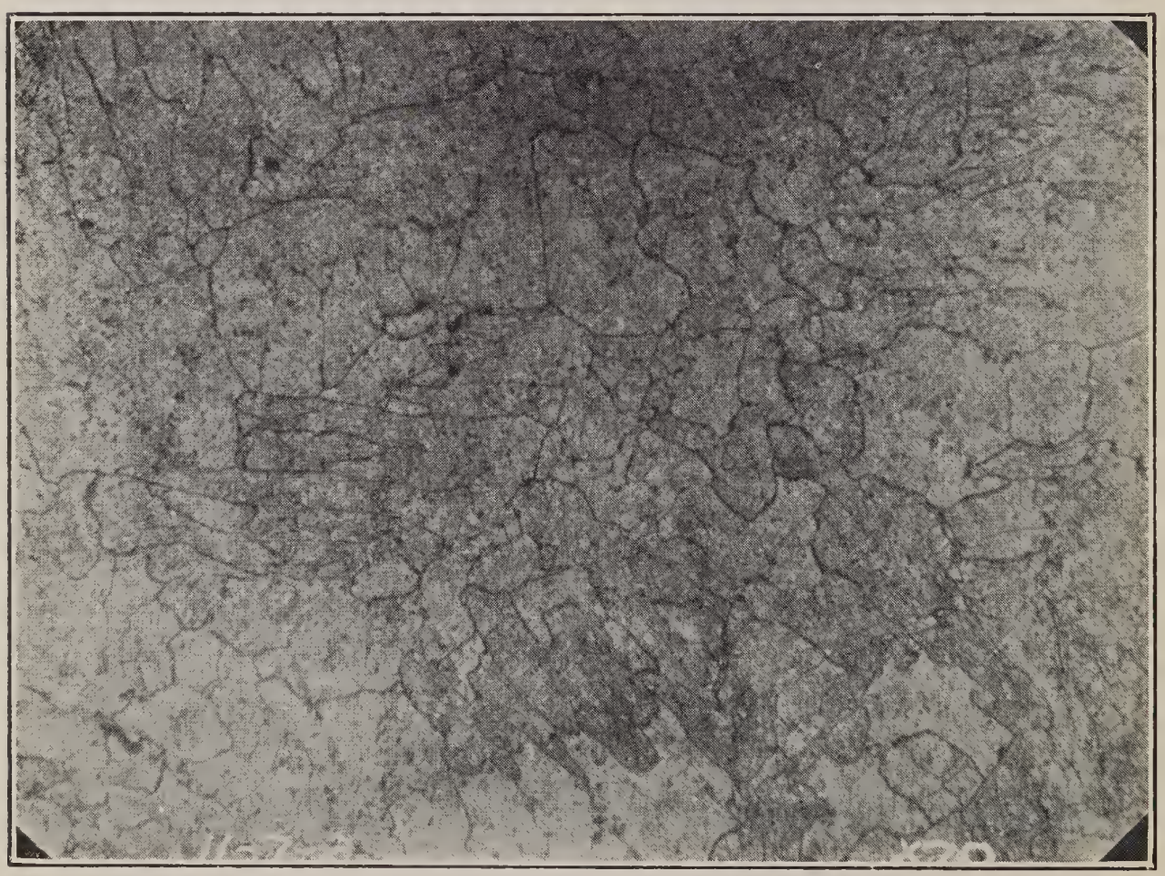


FIG. 42. × 70

FIG. 43. × 70

FIG. 44. × 70

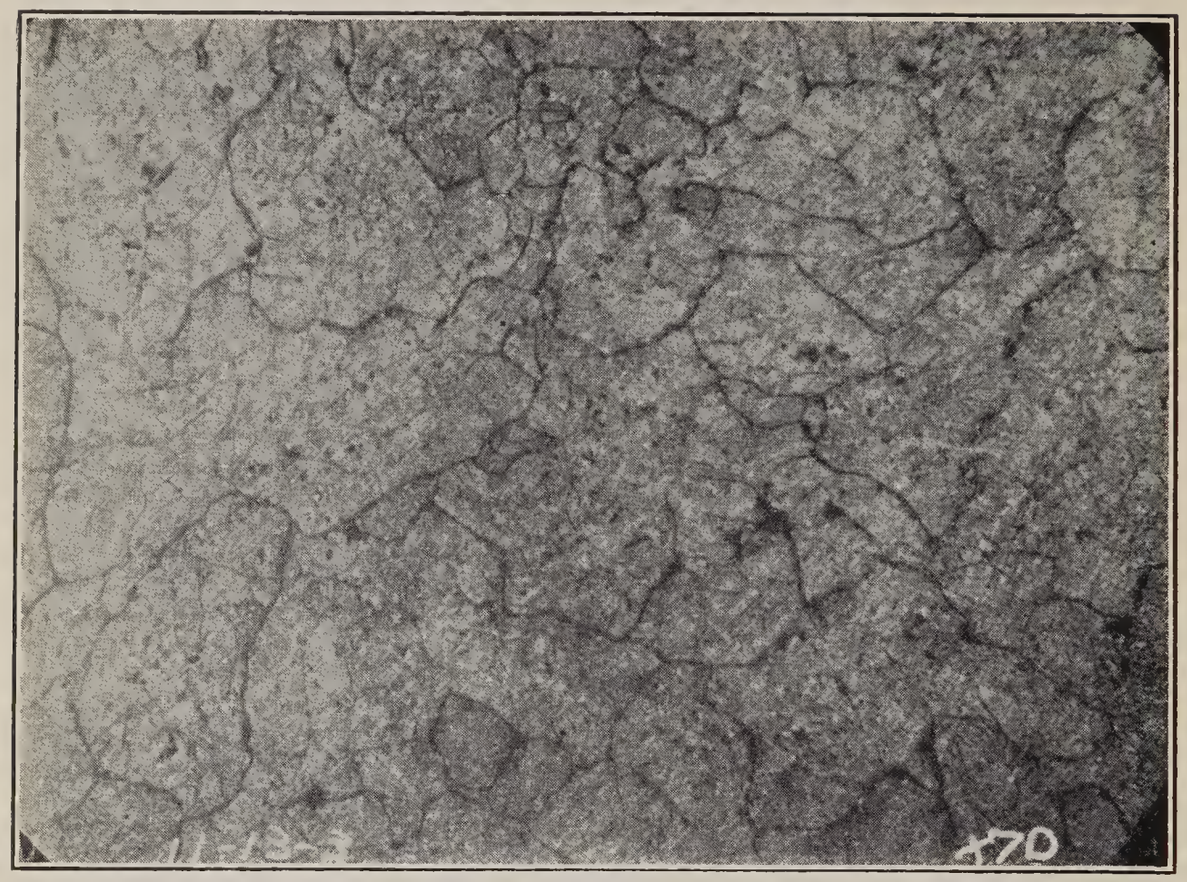


FIG. 45. × 70

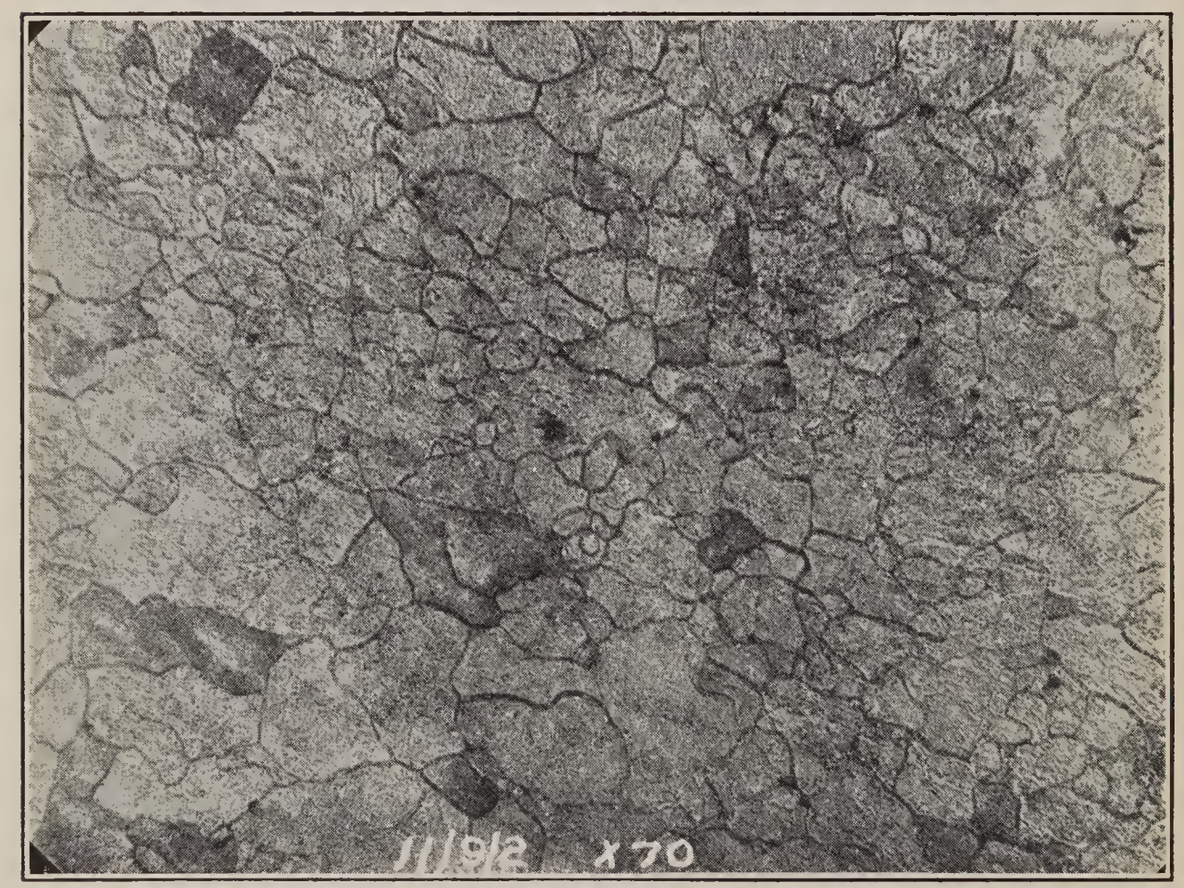


FIG. 46. × 70

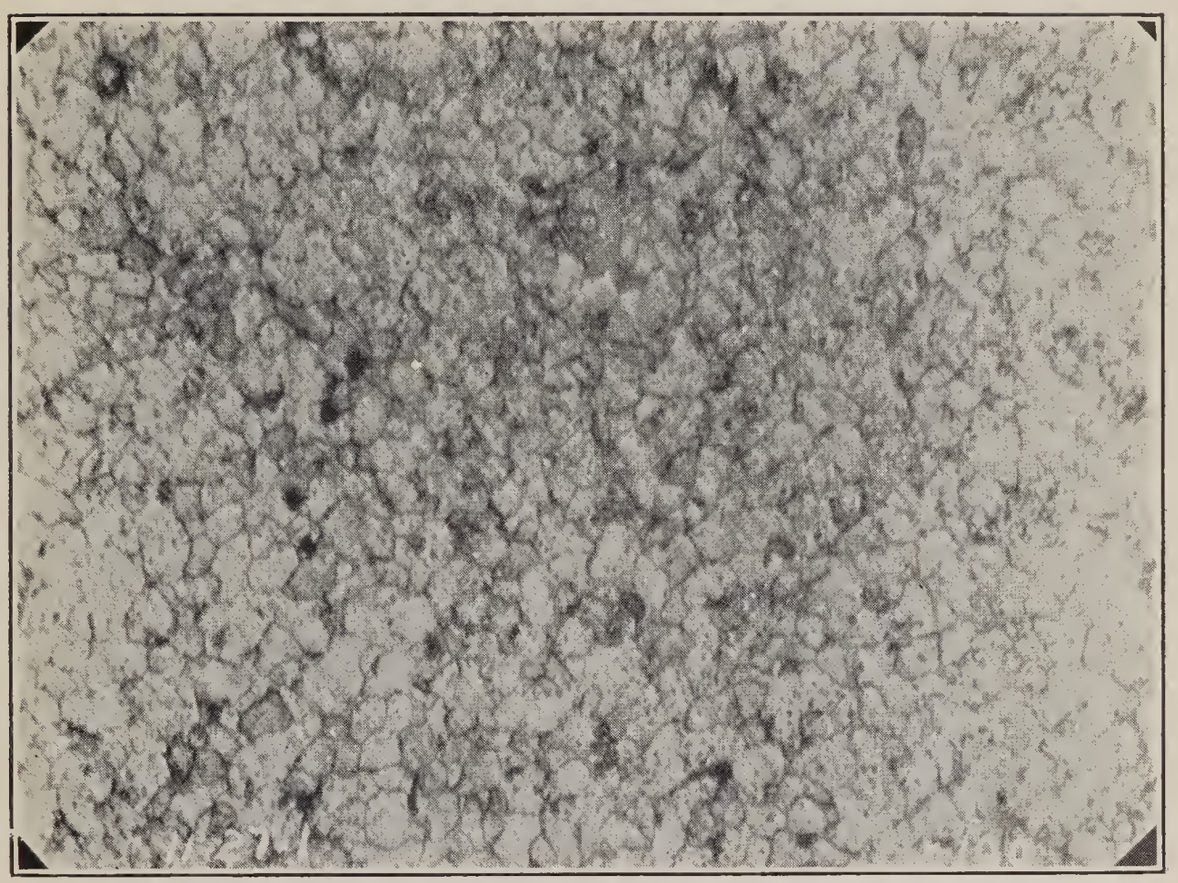


FIG. 47. × 100

FIG. 48. × 100

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

THE EFFECT OF ADDITION AGENTS IN THE ELECTRODEPOSITION OF IRON.

By O. P. Watts and M. H. Li.

The results set forth in this paper formed part of a thesis written by the junior author for the degree of Chemical Engineer at the University of Wisconsin, and are here presented as an addition to the rapidly growing literature dealing with the effects of small additions of foreign substances to solutions for the electrodeposition of metals.

Previous experience in refining iron had shown the senior author that, while an electrolyte containing only chlorides gave a much smoother deposit than one consisting of the sulphates of iron and ammonia, the iron produced rusted so badly after removal from the electrolyte that a pure chloride electrolyte was not considered practical.

It was found, however, that the admixture of some chloride with the sulphate electrolyte improved the smoothness of the deposit without causing excessive rusting of the iron produced.

When a solution of ferrous sulphate alone was used as an electrolyte its rapid oxidation caused the formation of excessive and harmful amounts of precipitate. The addition of 60 grams of ammonium sulphate per liter of solution considerably diminished this precipitate and resulted in the production of better cathodes than in its absence.

The electrolyte chosen as a basis for the addition of various substances consisted of 150 grams crystallized ferrous sulphate ($FeSO_4.7H_2O$) and 75 grams ferrous chloride ($FeCl_2.4H_2O$) per liter, and had a specific gravity of 1.125 at 20° C.

Fluosilicates and fluoborates have proved very successful for the deposition of lead and nickel, and a test of these electrolytes was therefore made for the deposition of iron. The solutions were prepared by dissolving iron in the respective acids and then neutralizing by ammonia.

A. Ferrous ammonium fluosilicate was electrolyzed with an anode of mild steel for 170 hours at 10 amperes per square foot (1.1 per sq. dm.) at room temperature (26° C.). The deposit was dark gray, streaky and very nodular. The electrolytic cell was half full of a white precipitate.

B. Ferrous ammonium fluoborate was electrolyzed similarly for 150 hours, with similar results as to deposit and electrolyte.

These electrolytes were very inferior to ferrous ammonium sulphate.

The next set of experiments consisted in a comparison of the effect of additions of the sulphates of ammonium, aluminum, magnesium and sodium to the above mentioned basic electrolyte (ferrous sulphate and chloride). The results are indicated in Table I.

TABLE I.

Time of electrolysis 90 hours, current density 1 ampere per sq. dm.

	Addition Agent	Result
C.	50 g. $(NH_4)_2SO_4$ per liter.	Deposit white, but pitted. Little precipitate in electrolyte.
D.	50 g. Na_2SO_4	Poor, gray and pitted deposit. Much precipitate.
E.	50 g. $MgSO_4$	Deposit gray, nodular and rusts badly. Much precipitate.
F.	50 g. $Al_2(SO_4)_3$	Deposit gray, streaked, and peeling off at top. Solution half filled with flucculent precipitate.

To prevent the formation of precipitates, 30 cc. of dilute sulphuric acid (1 volume of acid to 4 volumes of water) was added to each liter of electrolyte and the amounts of the sulphates increased to 120 grams. The results appear in Table II.

TABLE II.

Time, 140 hours, at 1 ampere per sq. dm.

	Addition Agent	Result
G.	120 g. $(NH_4)_2SO_4$ + 30 cc. dil. H_2SO_4	Deposit bright, but nodular. Solution clear and yellowish.
H.	120 g. Na_2SO_4 + 30 cc. dil H_2SO_4	Deposit gray and very nodular. Gas evolved at cathode. Solution clear.
I.	120 g. $MgSO_4$ + 30 cc. dil. H_2SO_4	Deposit dark gray with large nodules. Gas at cathode. Little precipitate.
J.	120 g. $Al_2(SO_4)_3$ + 30 cc. dil. H_2SO_4	Deposit smooth and white at first, but finally gray and nodular. It rusted badly. Solution half filled with precipitate.

Since none of the other sulphates compared favorably with ammonium sulphate as an addition agent, the last named was used in all electrolytes for testing what further improvement could be made by organic substances.

TABLE III.

Electrolyte: 150 g. $FeSO_4.7H_2O$, 75 g. $FeCl_2.4H_2O$, 120 g. $(NH_4)_2SO_4$ } per liter.

Current density 1 ampere per sq. dm. Amount of addition agent is in grams per liter, and if not soluble in water was added as an alcoholic solution.

No.	Addition Agent	Time in Hours	Deposit
1.	0.5 g. acetanilide	170	Good, bright, but slightly pitted.
2.	0.5 g. acetphenetedin	170	Fair, good color, but much pitted.
3.	0.5 g. amidol	240	Fair, good color, but pitted.
4.	10 g. ammonium acetate, 20 cc. dil sulphuric acid	120	Bad, black and worthless.
5.	23.4 g. ammonium citrate	120	Bad, dark and streaked.
6.	10 g. ammonium oxalate, 20 cc. dil. sulphuric acid	120	Excellent, bright and smooth.
7.	20 g. ammonium oxalate	170	Very good, but inferior to No. 6.
8.	40 g. ammonium oxalate	40	Poor, brittle and peeling, contaminated by yellow precipitate.
9.	10 g. ammonium oxalate	290	Excellent.
10.	12.3 g. ammonium tartrate	50	Poor, slightly nodular and peeling off.
11.	0.5 g. benzoic acid	100	Bad, nodular and greenish. Gas at cathode.
12.	1 g. *beta*-naphthol	170	Poor; deposit of good color, but badly pitted.
13.	0.5 g. boric acid	200	Poor; deposit of good color, but badly pitted.
14.	2 drops bromoform	170	Poor, deposit white but badly pitted.
15.	2 drops creosote, white	170	Poor, of good color, but pitted.
16.	1 g. dextrine	170	Very good, white and smooth.
17.	0.5 g. eikonogen	220	Poor, of good color, but badly pitted.
18.	3 drops eucalyptol	170	Fair, brilliant, but nodular.
19.	4 drops formaldehyde (40 percent)	240	Excellent, bright and smooth.
20.	4 drops formin	250	Excellent, bright, smooth and compact.
21.	0.5 g. gallic acid	170	Fair, streaky.
22.	0.5 g. gelatine	100	Bad, corrugated, pitted and nodular.
23	1 g. glucose	170	Good, slightly nodular.
24.	0.5 g. gum arabic	240	Poor, vertical streaks and grooves.
25.	0.5 g. gum copal	120	Poor, good color, but badly pitted.
26.	0.5 g. gum dammar	170	Poor, good color, but pitted.
27.	0.5 g. gum sandarac	170	Fair, brilliant, but pitted.
28.	1 g. gum tragacanth	100	Fair, brilliant, peels off.
29.	0.5 g. licorice	200	Poor, much pitted.

No.	Addition Agent	Time in Hours	Deposit
30.	...extract logwood	200	Poor, good color, but pitted.
31.	2 drops lysol	200	Bad, gray with very large pits.
32.	3 drops oil of cedar.	140	Poor, of good color, but pitted.
33.	8 cc. oil of cloves	150	Fair, of excellent color, but pitted.
34.	0.5 g. peptone	170	Bad, mossy.
35.	4 drops phenol	190	Excellent.
36.	2 drops pyridine	120	Poor, of fair color, but pitted.
37.	1 g. pyrocatechin	170	Excellent.
38.	1 g. pyrogallol	120	Bad, dark colored, rusts badly.
39.	0.6 g. pyrogallol	100	Poor, brilliant, but nodular.
40.	1 g. resorcine	170	Very good, white and smooth.
41.	0.5 g. resorcine	240	Very good, white, but slightly nodular.
42.	0.5 g. salicin	170	Poor, gray and pitted.
43.	1 g. salicylic acid	120	Bad, gray and rough, rusts badly.
44.	0.5 g. saponin	100	Bad, spongy and badly rusted.
45.	0.5 g. tannic acid	100	Poor, badly pitted.
46.	0.5 g. terpin hydrate	170	Fair, of good color, but many small pits.
47.	3 drops turkey red oil	170	Bad, dark and badly pitted.
48.	2 drops turpentine	170	Poor, light gray and badly pitted.

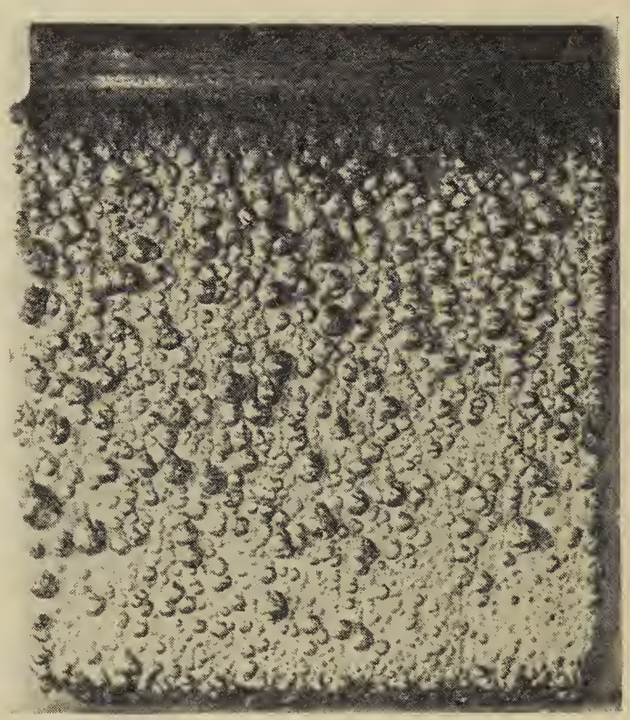


FIG. 1.

An objectionable tendency of electrolytic deposits is that they grow rough with increasing thickness, so that there is a limit, depending on the purpose for which the deposit is to be used, beyond which deposition cannot profitably be continued. Figure 1 shows a cathode of electrolytic iron a foot square and an inch or

more thick, a very good deposit. Cathodes of copper or lead of equal thickness are fully as rough and nodular. This might be called the natural state of electro-deposited metal. It is the function of the successful addition agent to remedy this roughness. A, 10 and I in Fig. 2 show the nodular structure produced by several addition agents, the original electrolyte giving deposits free from nodules until the cathode attains at least three times the thickness of those shown.

For convenience the addition agents used have been classified according to certain well-marked physical characteristics of the cathodes. In each class the order indicates the relative quality of the cathodes in respect to that characteristic, *e. g.*, under pitted deposits each is more pitted than the one following, while those italicised show this action to an exceptional degree.

Nodular Deposits: *11, 1,* 18, 41. Pitting caused by the clinging of bubbles of gas to the cathodes is a trouble to which thick cathodes of iron, nickel and zinc are subject. Copper and silver, whose discharge potentials in acid solutions are below that of hydrogen, are not subject to this trouble, so far as the writers have observed. 33, 47 and 31 in Fig. 2 show different degrees of pitting by gas bubbles. Although many of the addition agents are reported to cause pitting, there is a probability that experiments covering a longer period would have eliminated the pitting in several cases, for this has been found to grow less the longer electrolysis is continued, and seemingly it does not always keep step with exhaustion of the addition agent.

Pitted deposits: *31, C, 25, 47, 48,* 17, 13, 42, 34, 46, 12, 21, 33, *27,* 36, 3, 1, 29, 26, 30, 32, 15, *22.*

Vertical grooves or striations is another trouble occasionally met with. Cathodes *24* and 5 were so afflicted.

"Brighteners" for silver and brass solutions have long been known among platers. Several addition agents produced bright deposits of iron, but these were extremely hard and brittle, and usually cracked and curled off from the starting sheet.

Bright deposits: *28, 18, 27,* 40, 8.

Several addition agents caused a badly rusted deposit, in the worst cases consisting entirely of iron rust.

Rusted deposits: *44, 11,* 1, E, H, 43, 38, F, D, 5, J.

The color of the electrolyte at the end of the test was closely

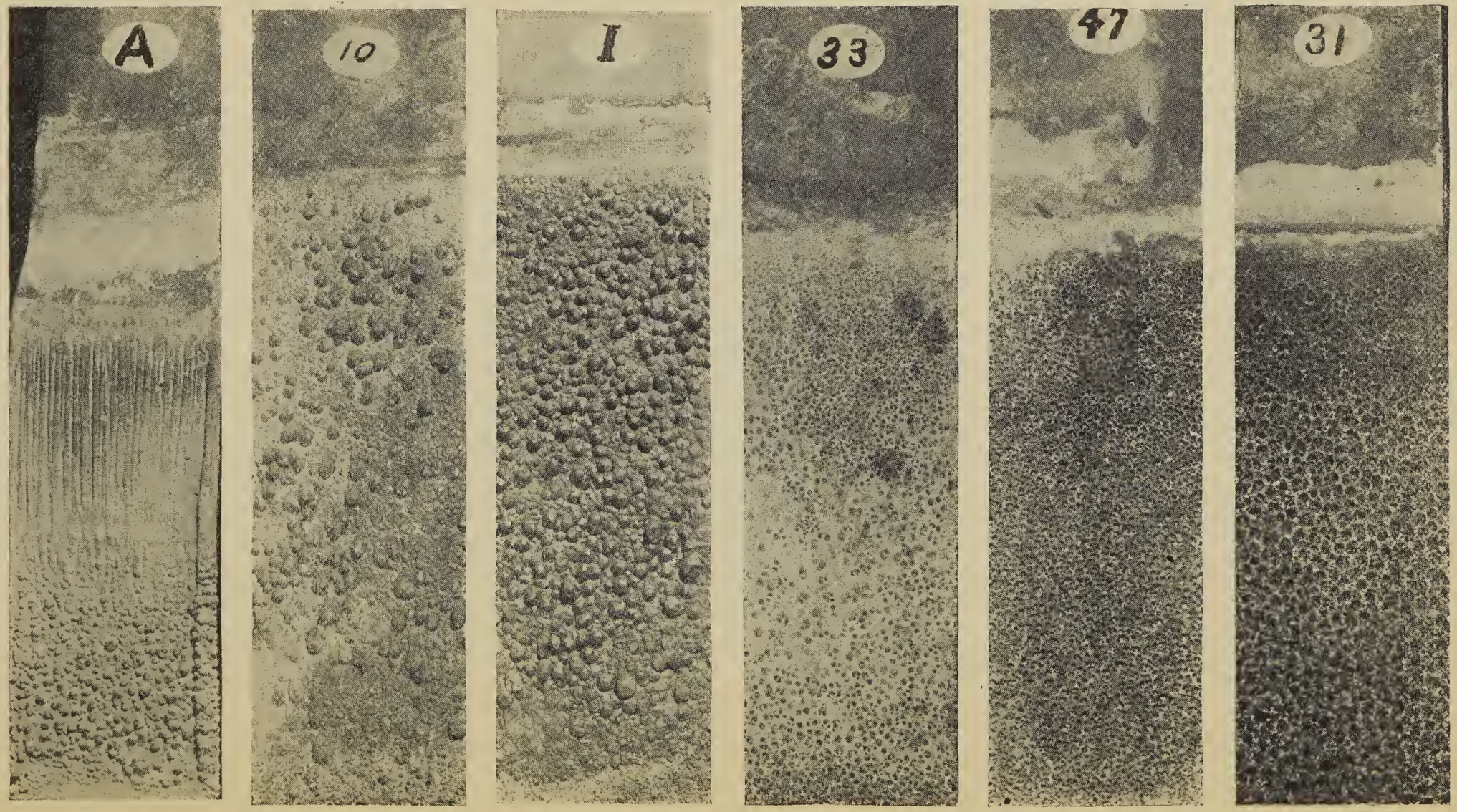


FIG. 2.

related to the quality of metal produced. A yellowish-green electrolyte almost invariably gave clean metal of a fine color, even though it might be too badly pitted to allow of the practical use of that particular electrolyte. A dark electrolyte fouled by much green precipitate usually yielded very bad looking mteal.

Yellowish-green electrolyte with little precipitate: 6, 7, 13, 15, 18, 19, 23, 25, 26, 27, 29, 30, 32, 33, 35, 36, 40, 45, 47, 48.

Ditto, with much precipitate: 2, 17.

Greenish electrolyte with little precipitate: 1, 3, 10, 12, 22, 31, 34, 40, 43, 46.

Ditto, with much precipitate: 20.

Bluish or dark green: 4, 5, 11, 14, 16, 21, 24, 28.

In order to test the best addition agents more thoroughly they were run continuously at 10 amperes per square foot for 21 to 30 days in series with a cell containing the electrolyte without any organic addition agent. The results are given in Table IV.

TABLE IV.

No.	Addition Agent	Days	Deposit
49.	None	30	Excellent, silvery, $\frac{7}{16}$-inch thick, slightly nodular.
50.	6 g. ammonium oxalate	30	Excellent, silvery and smooth. The best cathode of all.
51.	0.6 g. formin or hexamethylenetetramine	30	Excellent, bright and compact Slightly inferior to No. 50.
52.	0.5 g. resorcine	30	Very good, bright and solid, but slightly nodular near bottom.
53.	0.5 g. dextrine	30	Fair, excellent for first three weeks, then vertical grooves developed.
54.	4 drops formalin	21	Excellent, slightly nodular on the lower part.
55.	0.5 g. glucose	21	Fair, nodular near bottom.
56.	2 drops phenol	21	Excellent, white and solid, but with a few nodules near the bottom.
57.	0.2 g. tragacanth	21	Very good, slightly grooved, and thick on the edges.

The quality of metal in all of these deposits was excellent, and the only choice lay in smoothness and freedom from nodular structure.

Arranged in order of excellence, they are: *50, 51,* 56, 54, 49. The first two were distinctly superior to No. 49, which contained no addition agent. The others so closely resembled No. 49 that it is doubtful if these addition agents caused any improvement.

These experiments show that two organic addition agents, ammonium oxalate and formin, are capable of improving upon the remarkably smooth and satisfactory deposit given by the original electrolyte.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

INDEX.

PAGE.

Addicks, L.—*Discussion*.....205 *et seq.*
Addicks, L.—The Power Problem in the Electrolytic Deposition of Metals 65
Addition Agents in the Deposition of Zinc—O. P. Watts and A. C. Shape 291
Addition Agents in the Electrodeposition of Iron, The Effect of—O. P. Watts and M. H. Li.....529
Advantages of Southeastern Alaska for Hydro-Electrochemical Industries—W. P. Lass.....179
Agents, Addition, in the Deposition of Zinc from Zinc Sulphate Solution—O. P. Watts and A. C. Shape.....291
Agents, Addition, The Effect, in the Electrodeposition of Iron—O. P. Watts and M. H. Li.....529
Alaska, Southeastern, Advantages of, for Hydro-Electrochemical Industries—W. P. Lass.....179
A Microscopic Study of Electrolytic Iron—O. W. Storey.....489
A New Method for the Determination of Free Cyanide in Electro-Plating Solutions—G. E. F. Lundell 369
Annual Report of the Board of Directors..... 4
Annual Report of the Secretary..... 6
Annual Report of the Treasurer..... 9
A Railway Track Cell—E. L. Marshall.....467
Aspects, Some Economic and Aesthetic, of Electrochemistry—E. F. Roeber 17
Bancroft, W. D.—*Discussion*.....130 *et seq.*
Bancroft, W. D., and Weiser, H. B.—Electrolytic Flames.....121
Bennett, C. W.—*Discussion*.....346
Bennett, C. W., and Davison, A. W.—Electrolytic Deposition of Brass on the Rotating Cathode 347
Bennett, C. W., Kenny, H. C., and Dugliss, R. P.—Electrodeposition of Nickel 335
Beutner, R.—New Cell Arrangement for Direct Determination of the "Free Energy" 441
Board of Directors, Annual Report of..... 4
Board of Directors, Minutes of the Meeting of..... 9
Brass, Electrolytic Deposition of, on the Rotating Cathode—C. W. Bennett and A. W. Davison.....347
Cadmium, Electrodeposition of, I—F. C. Mathers and H. M. Marble...297
Cadmium, Electrodeposition of, II—F. C. Mathers and H. M. Marble..319

PAGE
Castings, Electric Steel—C. A. Hansen....133
Cathode, Rotating, Electrolytic Deposition of Brass on the—C. W. Bennett and A. W. Davison....347
Cell, Track, A Railway—E. L. Marshall....467
Characteristics of Electrical Energy as Affecting Chemical Industries —C. P. Steinmetz 29
Chemical Industries, Characteristics of Electrical Energy as Affecting —C. P. Steinmetz.... 29
Chuquicamata, Chile, Leaching and Electrolytic Treatment of Copper Ores at—E. A. C. Smith....193
Clarke, E. B.—*Discussion* ....158 *et seq.*
Clarke, E. B.—Electric Furnaces for Steel Making....139
Conduction, Electrical, at High Temperatures and Its Measurement— E. F. Northrup....373
Cone, E. F.—*Discussion*....154
Copper Ores, Leaching and Electrolytic Treatment of, at Chuquicamata, Chile—E. A. C. Smith....193
Copper Ores, The Hydroelectric Treatment of—R. R. Goodrich....207
Copper Refinery, Metal Inventory in an Electrolytic—R. W. Deacon..255
Copper Tailings, Leaching of—R. Gahl....243
Cowles, A. H.—*Discussion*....158
Crosby, E. L.—*Discussion*....152 *et seq.*
Current, Direct, for Electrochemical Processes, Sources of—F. D. Newbury 85
Current, Electric Furnace, Regulators—R. Turnbull.... 97
Cyanide, Free, in Electroplating Solutions, A New Method for the Determination of—G. E. F. Lundell....369
Davison, A. W., and Bennett, C. W.—Electrolytic Deposition of Brass on the Rotating Cathode....347
Deacon, R. W.—Metal Inventory in an Electrolytic Copper Refinery...255
Deposition, Electrolytic, of Brass on the Rotating Cathode—C. W. Bennett and A. W. Davison....347
Deposition, Electrolytic, of Metals, The Power Problem in— L. Addicks 65
Deposition, Electrolytic, of Metals, The Power Problem in—H. E. Longwell 73
Deposition, Electrolytic, of Zinc—J. W. Richards....281
Deposition of Zinc from Zinc Sulphate Solution, Addition Agents in— O. P. Watts and A. C. Shape 291
Determination of Free Cyanide in Electroplating Solutions, A New Method for the—G. E. F. Lundell....369
Determination of the "Free Energy," New Cell Arrangement for Direct—R. Beutner 441
Direct Current, Sources of, for Electrochemical Processes—F. D. Newbury 85

PAGE
Discussion, General, on Power Problems in Electrochemistry.....107
Dugliss, R. P., Bennett, C. W., and Kenny, H. C.—Electrodeposition of Nickel 335
Economies in the Use of Energy in Electric Furnaces—F. A. J. FitzGerald 53
Effect of Addition Agents in the Electrodeposition of Iron—O. P. Watts and M. H. Li.....529
Electric Furnace Current Regulators—R. Turnbull..... 97
Electric Furnaces for Steel Making—E. B. Clarke.....139
Electric Furnaces, Some Economies in the Use of Energy in—F. A. J. FitzGerald 53
Electric Furnace Work, Power in—W. S. Horry..... 59
Electric Steel Castings—C. A. Hansen.....133
Electric Zinc Smelting—W. R. Ingalls.....169
Electrical Conduction at High Temperatures and Its Measurement—E. F. Northrup 373
Electrical Energy, Characteristics of, as Affecting Chemical Industries —C. P. Steinmetz 29
Electrical Properties of Silver Sulphide, Laboratory Notes on Some —F. A. J. FitzGerald 393
Electrochemical Processes, Sources of Direct Current for—F. D. Newbury 85
Electrochemistry, Power Problems in, General Discussion on.....107
Electrochemistry, Some Economic and Aesthetic Aspects of—E. F. Roeber 17
Electrodeposition of Cadmium, I—F. C. Mathers and H. M. Marble...297
Electrodeposition of Cadmium, II—F. C. Mathers and H. M. Marble..319
Electrodeposition of Iron, The Effect of Addition Agents in the—O. P. Watts and M. H. Li.....529
Electrodeposition of Nickel—C. W. Bennett, H. C. Kenny and R. P. Dugliss 335
Electrolytic Copper Refinery, Metal Inventory in—R. W. Deacon.....255
Electrolytic Deposition of Brass on the Rotating Cathode—C. W. Bennett and A. W. Davison.....347
Electrolytic Deposition of Metals, The Power Problem in—L. Addicks 65
Electrolytic Deposition of Metals, The Power Problem in—H. E. Longwell 73
Electrolytic Deposition of Zinc—J. W. Richards.....281
Electrolytic Flames—W. D. Bancroft and H. B. Weiser.....121
Electrolytic Iron, A Microscopic Study of—O. W. Storey.....489
Electrolytic Treatment of Copper Ores at Chuquicamata, Chile, Leaching and—E. A. C. Smith 193
Electroplating Solutions, A New Method for the Determination of Free Cyanide in—G. E. F. Lundell.....369

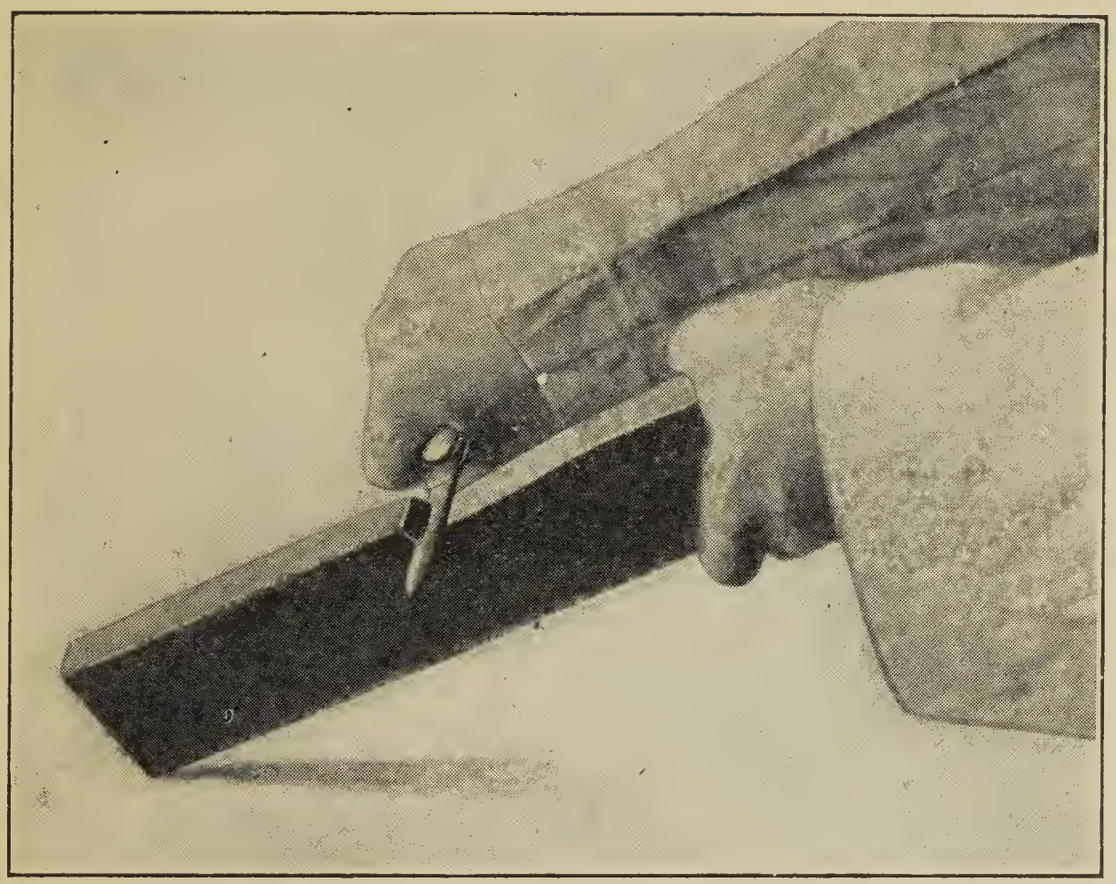
PAGE
Energy, Electrical, Characteristics of, as Affecting Chemical Industries —C. P. Steinmetz 29
Energy in Electric Furnaces, Some Economies in the Use of—F. A. J. Fitzgerald 53
Experiments on White Lead—R. S. Owens.....477
Fink, C. G.—*Discussion*.....390
FitzGerald, F. A. J.—Laboratory Notes on Some Electrical Properties of Silver Sulphide 393
FitzGerald, F. A. J.—Some Economies in the Use of Energy in Electric Furnaces 53
Flames, Electrolytic—W. D. Bancroft and H. B. Weiser.....121
Frank, K. G.—*Discussion*.....149 *et seq.*
Free Cyanide in Electroplating Solutions, A New Method for the Determination of—G. E. F. Lundell.....369
"Free Energy," New Cell Arrangement for Direct Determination of— R. Beutner 441
Furnace, Electric, Current Regulators—R. Turnbull..... 97
Furnaces, Electric, for Steel Making—E. B. Clarke.....139
Furnaces, Electric, Some Economies in the Use of Energy in—F. A. J. FitzGerald 53
Furnace Work, Electric, Power in—W. S. Horry..... 59
Gahl, R.—Leaching of Copper Tailings.....243
General Discussion on Power Problems in Electrochemistry.....107
Goodrich, R. R.—The Hydroelectric Treatment of Copper Ores.....207
Guests and Members Registered at the Twenty-fifth Meeting..... 11
Hambuechen, C.—*Discussion*.....130 *et seq.*
Hansen, C. A.—*Discussion*.....108 *et seq.*, 149 *et seq.*
Hansen, C. A.—Electric Steel Castings.....133
Hering, C.—*Discussion*.....117 *et seq.*, 289 *et seq.*
Hess, H.—*Discussion*.....149 *et seq.*
Hibbard, H. D.—*Discussion*.....145 *et seq.*
Hitchcock, C. N.—Polarization Single Potentials.....415
Horry, W. S.—Power in Electric Furnace Work..... 59
Humbert, E.—*Discussion*.....146 *et seq.*
Hydroelectric Treatment of Copper Ores—R. R. Goodrich.....207
Hydro-Electrochemical Industries, Advantages of Southeastern Alaska for—W. P. Lass 179
Improvements in the Metallurgy of Zinc—G. C. Stone.....161
Ingalls, W. R.—*Discussion*.....177 *et seq.*
Ingalls, W. R.—Electric Zinc Smelting.....169
Inventory, Metal, in an Electrolytic Copper Refinery—R. W. Deacon...255
Iron, Electrodeposition of, The Effect of Addition Agents in—O. P. Watts and M. H. Li.....529
Iron, Electrolytic, A Microscopic Study of—O. W. Storey.....489
Johnson, W. McA.—*Discussion*.....175 *et seq.*

PAGE
Kenny, H. C., Bennett, C. W., and Dugliss, R. P.—Electrodeposition of Nickel 335
Laboratory Notes on Some Electrical Properties of Silver Sulphide—F. A. J. FitzGerald 393
Lass, W. P.—Advantages of Southeastern Alaska for Hydro-Electrochemical Industries 179
Leaching and Electrolytic Treatment of Copper Ores at Chuquicamata, Chile—E. A. C. Smith 193
Leaching of Copper Tailings—R. Gahl.....243
Lead, White, Experiments on—R. S. Owens.....477
Lidbury, F. A.—*Discussion*.....109 *et seq.*, 153, 289 *et seq.*, 366 *et seq.*
Lidbury, F. Austin, Portrait of.....*Frontispiece*
Li, M. H., and Watts, O. P.—The Effect of Addition Agents in the Electrodeposition of Iron 529
Lincoln, P. M.—*Discussion*.....113 *et seq.*, 391 *et seq.*
Longwell, H. E.—The Power Problem in the Electrolytic Deposition of Metals 73
Lundell, G. E. F.—A New Method for the Determination of Free Cyanide in Electroplating Solutions 369
Mainwaring, W. D.—*Discussion*.....155 *et seq.*
Marble, H. M., and Mathers, F. C.—Electrodeposition of Cadmium, I..297
Marble, H. M., and Mathers, F. C.—Electrodeposition of Cadmium, II.319
Marshall, E. L.—A Railway Track Cell.....467
Mathers, F. C.—*Discussion*.....333
Mathers, F. C., and Marble, H. M.—Electrodeposition of Cadmium, I..297
Mathers, F. C., and Marble, H. M.—Electrodeposition of Cadmium, II.319
Measurement of Electrical Conduction at High Temperatures—E. F. Northrup 373
Meeting of the Board of Directors, Minutes of..... 9
Members and Guests Registered at the Twenty-fifth Meeting..... 11
Members Elected and Qualified September, 1913-March, 1914..... 14
Metal Inventory in an Electrolytic Copper Refinery—R. W. Deacon....255
Metallurgy of Zinc, Improvements in the—G. C. Stone.....161
Metals, Electrolytic Deposition of, The Power Problem in—L. Addicks. 65
Metals, Electrolytic Deposition of, The Power Problem in—H. E. Longwell 73
Microscopic Study of Electrolytic Iron—O. W. Storey.....489
Minutes of the Meeting of the Board of Directors..... 9
Newbury, F. D.—Sources of Direct Current for Electrochemical Processes 85
New Cell Arrangement for Direct Determination of the "Free Energy" —R. Beutner 441
New Method for the Determination of Free Cyanide in Electroplating Solutions—G. E. F. Lundell 369

PAGE
Nickel, Electrodeposition of—C. W. Bennett, H. C. Kenny and R. P. Dugliss 335
Northrup, E. F.—*Discussion* ..... 131, 390 *et seq.*
Northrup, E. F.—Electrical Conduction at High Temperatures and Its Measurement 373
Notes, Laboratory, on Some Electrical Properties of Silver Sulphide—F. A. J. FitzGerald 393
Notes on Power Transmission and Transmission Economics—P. W. Sothman 43
Owens, R. S.—Experiments on White Lead 477
Petinot, N.—*Discussion* 107
Polarization Single Potentials—C. N. Hitchcock 415
Portrait of F. Austin Lidbury ..... *Frontispiece*
Power in Electric Furnace Work—W. S. Horry 59
Power Problems in Electrochemistry, General Discussion on 107
Power Problem in the Electrolytic Deposition of Metals—L. Addicks .. 65
Power Problem in the Electrolytic Deposition of Metals—H. E. Longwell 73
Power Transmission and Transmission Economics, Notes on—P. W. Sothman 43
Pring, J. N.—*Discussion* ..... 294 *et seq.*
Proceedings of the Twenty-fifth General Meeting 1
Processes, Electrochemical, Sources of Direct Current for—F. D. Newbury 85
Properties, Electrical, of Silver Sulphide, Laboratory Notes on Some—F. A. J. FitzGerald 393
Railway Track Cell—E. L. Marshall 467
Regulators, Electric Furnace Current—R. Turnbull 97
Report, Annual, of the Board of Directors 4
Report, Annual, of the Secretary 6
Report, Annual, of the Treasurer 9
Richards, J. W.—*Discussion* ..... 119 151 *et seq.*, 205 *et seq.*, 290, 390 *et seq.*
Richards, J. W.—The Electrolytic Deposition of Zinc 281
Roeber, E. F.—*Discussion* 115
Roeber, E. F.—Some Economic and Aesthetic Aspects of Electrochemistry 17
Rotating Cathode, Electrolytic Deposition of Brass on the—C. W. Bennett and A. W. Davison 347
Roush, G. A.—*Discussion* 367
Schluederberg, C. G.—*Discussion* 153
Secretary, Annual Report of 6
Shape, A. C., and Watts, O. P.—Addition Agents in the Deposition of Zinc from Zinc Sulphate Solution 291
Silver Sulphide, Laboratory Notes on Some Electrical Properties of—F. A. J. FitzGerald 393

PAGE
Single, Polarization, Potentials—C. N. Hitchcock....415
Smelting, Electric Zinc—W. R. Ingalls....169
Smith, E. A. C.—*Discussion*....205 *et seq.*
Smith, E. A. C.—Leaching and Electrolytic Treatment of Copper Ores at Chuquicamata, Chile....193
Solutions, Electroplating, A New Method for the Determination of Free Cyanide in—G. E. F. Lundell....369
Some Economic and Aesthetic Aspects of Electrochemistry—E. F. Roeber....17
Some Economies in the Use of Energy in Electric Furnaces—F. A. J. FitzGerald....53
Sothman, P. W.—*Discussion*....115 *et seq.*
Sothman, P. W.—Notes on Power Transmission and Transmission Economics....43
Sources of Direct Current for Electrochemical Processes—F. D. Newbury....85
Steel Castings, Electric—C. A. Hansen....133
Steel Making, Electric Furnaces for—E. B. Clarke....139
Steinmetz, C. P.—Characteristics of Electrical Energy as Affecting Chemical Industries....29
Steinmetz, C. P.—*Discussion*....111 *et seq.*
Stone, G. C.—Improvements in the Metallurgy of Zinc....161
Storey, O. W.—A Microscopic Study of Electrolytic Iron....489
Study, Microscopic, of Electrolytic Iron—O. W. Storey....489
The Effect of Addition Agents in the Electrodeposition of Iron—O. P. Watts and M. H. Li....529
The Electrolytic Deposition of Zinc—J. W. Richards....281
The Hydroelectric Treatment of Copper Ores—R. R. Goodrich....207
The Power Problem in the Electrolytic Deposition of Metals—L. Addicks....65
The Power Problem in the Electrolytic Deposition of Metals—H. E. Longwell....73
Transmission Economics and Power Transmission, Notes on—P. W. Sothman....43
Transmission, Power, and Transmission Economics, Notes on—P. W. Sothman....43
Treasurer, Annual Report of....9
Treatment, Electrolytic, and Leaching, of Copper Ores at Chuquicamata, Chile—E. A. C. Smith....193
Treatment, Hydroelectric, of Copper Ores—R. R. Goodrich....207
Tucker, S. A.—*Discussion*....131
Turnbull, R.—*Discussion*....107 *et seq.*
Turnbull, R.—Electric Furnace Current Regulators....97
Use of Energy in Electric Furnaces, Some Economies in—F. A. J. FitzGerald....53

PAGE
Watts, O. P. and Li, M. H.—The Effect of Addition Agents in the Electrodeposition of Iron 529
Watts, O. P., and Shape, A. C.—Addition Agents in the Deposition of Zinc from Zinc Sulphate Solution.....291
Watts, O. P.—*Discussion*.....295 *et seq.*, 331 *et seq.*, 345 *et seq.*
Weiser, H. B. and Bancroft, W. D.—Electrolytic Flames.....121
White Lead, Experiments on—R. S. Owens.....477
Whitney, W. R.—*Discussion*.....132
Zinc, Deposition of, from Zinc Sulphate Solution, Addition Agents in..291
Zinc, Electrolytic Deposition of—J. W. Richards.....281
Zinc, Metallurgy of, Improvements in the—G. C. Stone.....161
Zinc Smelting, Electric—W. R. Ingalls 169



Design in Electrodes

Rods and plates of pure Acheson-Graphite are easier to machine than the softest iron, and may be finished with the same degree of nicety, thus permitting special designs. Threads may be cut, holes drilled and tapped, or the Electrodes planed, sawed or shaped in any way desired. Since the Electrodes are practically chemically pure graphite throughout, there can be nothing to interfere with the use of plane, drill, saw, brace and bit, or the pocket knife. Threads are cut with the regular tap and die, or on the lathe and any of the machine operations—drilling, planing or cutting off—is accomplished with equal facility, using either wood-working or metal-working tools.

We shall be very glad to give you all possible information relative to Acheson-Graphite Electrodes and their use in electrolytic or electrothermic processes. Ask us to send you any of the following booklets of interest to you.

Booklet	**449-I**	**Electrolytic Work**	**(in English)**
"	**452-I**	**Electrothermic "**	**(" ")**
"	**450-I**	**Electrolytic "**	**(in French)**
"	**453-I**	**Electrothermic "**	**(" ")**
"	**451-I**	**Electrolytic "**	**(in German)**
"	**454-I**	**Electrothermic "**	**(" ")**

ACHESON TRADE ELECTRIC FURNACE MARK GRAPHITE

International Acheson Graphite Company

Niagara Falls, N.Y. Niagara Falls, Ont.

Dovenhof 120, Hamburg 8, Germany

Cromil Engineering Co., Milburn House, Newcastle-on-Tyne, England

The Roessler & Hasslacher Chemical Co.

MANUFACTURING AND
IMPORTING

CHEMISTS

SPECIALTIES:

Chloroform

Cyanide

Peroxides

Perborates

Oxone

Hydrone

Chemical Works

PERTH AMBOY, N.J.

Electrolytical Works

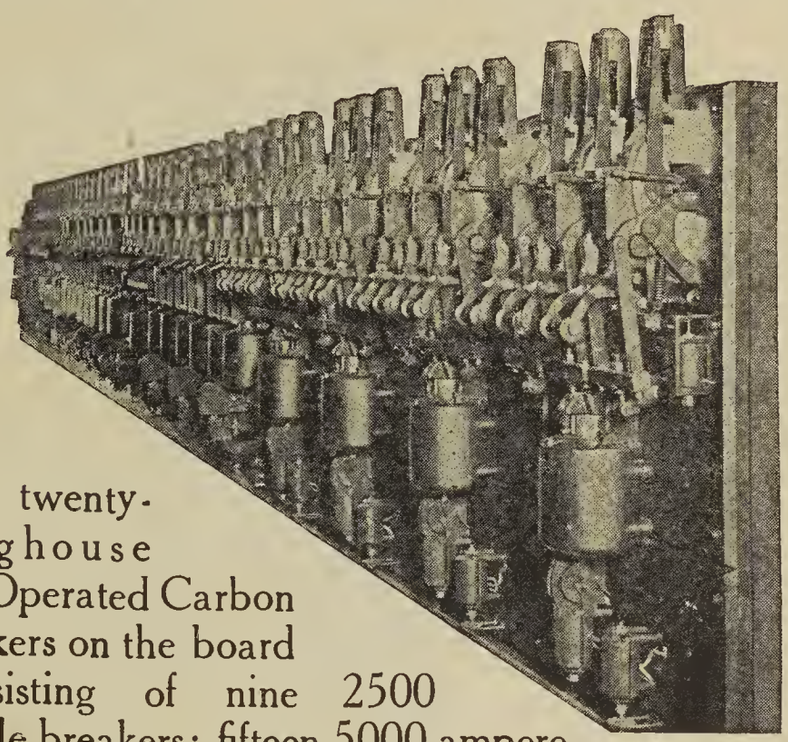
(Niagara Electro-Chemical Co.)

NIAGARA FALLS, N.Y.

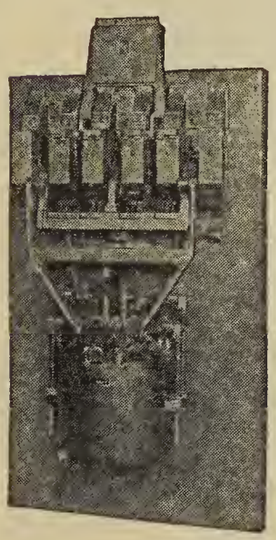
---

100 William Street, New York

Heavy Circuit Breaker Equipment for Large Capacity Electrolytic Reduction



There are twenty-six Westinghouse Electrically-Operated Carbon Circuit Breakers on the board shown, consisting of nine 2500 ampere, 3-pole breakers; fifteen 5000 ampere single-pole breakers; and two 10,000 ampere single-pole breakers. This breaker equipment controls a total of approximately 22,500 KW at 500 volts direct current.



We also illustrate one of the largest circuit breakers ever built. It is electrically operated and has a capacity of 24,000 amperes at 500 volts. Note the rugged construction and compact arrangement; the wide spread of the copper brushes that insures continuous operation with low temperature rise.

This switchboard and the 24,000 ampere breaker, illustrated, are now in operation in the plant of the largest aluminum company in the world.

Westinghouse Electric & Manufacturing Co.

East Pittsburgh, Pa.

Sales Offices in Forty-five American Cities

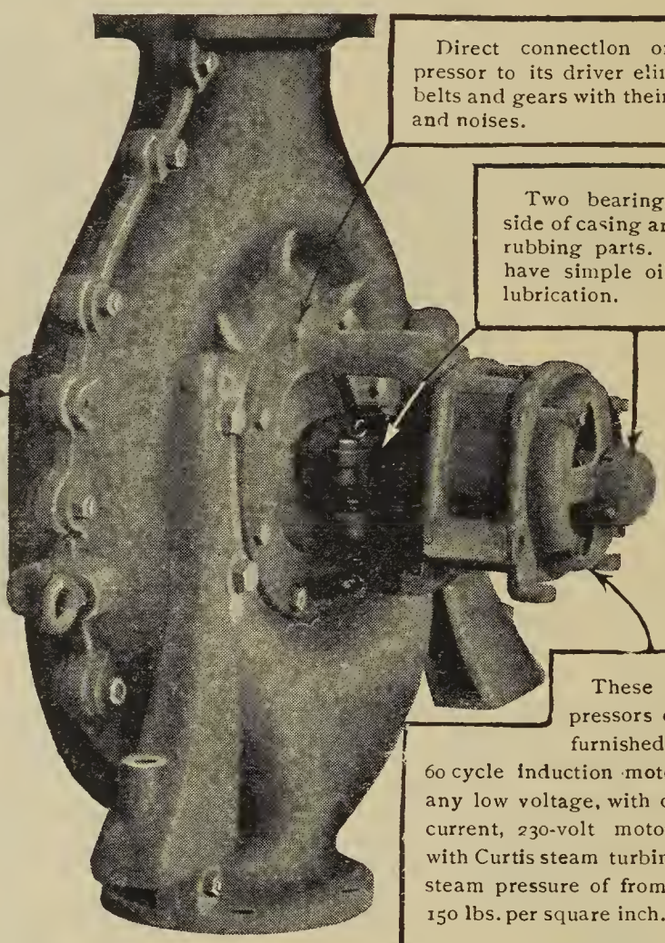
Air Compressors

for oil or gas burning furnaces ; cupola blowing ; pneumatic conveying systems ; refrigerating plants, in fact, wherever low or medium pressure air is wanted in large volumes and at an even non-pulsating flow.

Compressor unit is highly efficient, maintaining its efficiency indefinitely as there is no wear on compressor parts.

Machine inherently regulates for practically constant pressure obviating the necessity for speed regulating devices as used on some types of blowers.

Load on motor automatically decreases with reduction of volume of air used, due to inherent characteristic of compressor.



Direct connection of compressor to its driver eliminates belts and gears with their losses and noises.

Two bearings outside of casing are only rubbing parts. They have simple oil ring lubrication.

These compressors can be furnished with 60 cycle induction motors of any low voltage, with direct-current, 230-volt motors, or with Curtis steam turbines for steam pressure of from 80 to 150 lbs. per square inch.

Very small floor space is required. Compressor intake and outlet openings are diametrically opposite and may be furnished with intake at bottom, left, top or right facing driver.

Bulletin A-4084 gives complete description and list of sizes. Our nearest office will send it

General Electric Company

Largest Electrical Manufacturer in the World

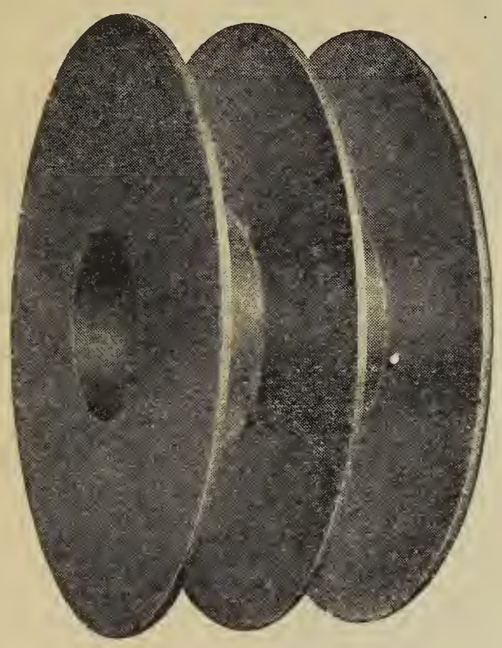
General Office : Schenectady, N. Y.

DISTRICT OFFICES IN

BOSTON, MASS. NEW YORK, N. Y. PHILADELPHIA, PA. ATLANTA, GA.
CINCINNATI, OHIO CHICAGO, ILL. DENVER, COLO. SAN FRANCISCO, CAL.

Sales Offices in all Large Cities

4996



Profit by This Example of Difficult Moulding

Solenoid Coil Spool, moulded in one piece. Diameter, $4\frac{3}{8}$ inches; length, 2 inches. Flanges, $\frac{1}{16}$ inch thick. Moulded by The Stevenson Company, Pittsburgh, Pa.

NOTE THE REQUIREMENTS

The flanges had to be thin to economize space, yet strong to support the great weight of copper wire; the wall of the barrel had to be thin to increase efficiency; yet able to withstand shock.

The material had to be heat-resisting to allow for overload and continuous operation. It had to be a good insulator and not absorb moisture or oil. The dimensions had to be accurate and the pieces uniform.

BAKELITE

MET THE SPECIFICATIONS OF THE DESIGNING ENGINEER

BAKELITE is continually meeting exacting specifications—send us yours with blue prints.

Booklet describing Bakelite Moulded Insulation is yours for the asking

GENERAL BAKELITE COMPANY

100 WILLIAM ST. NEW YORK

3

BETTER CASTINGS

of Iron, Steel, Brass, German Silver, Monel Metal, Aluminum and Composition are produced with the aid of our

CARBON-FREE METALS and ALLOYS

We have a pure carbon-free metal or alloy for practically every purpose and these are supplied in the most convenient forms to use. There are a great many cases where it is much better and more economical to use **Carbon-free** Metals and Alloys than metals containing carbon.

We have made a careful investigation of these cases and in our Pamphlet No. 20-X, which every metallurgist and foundryman should have, we have endeavored to cover the subject fully. If you have not yet written for this pamphlet do so without delay. A postal will bring it to you by return mail.

Here are a few of the metals and alloys which we carry in stock. You probably need one or more of them. Let us tell you why and how.

Manganese Tin, 50-50%
Manganese Zinc, 20-80%
Manganese Copper, 30-70%
Pure Manganese, 98%
Ferro Molybdeum, 80%
Pure Chromium, 99%
Molybdenum, 99%
Chromium Molybdenum, 80% Molybdenum
Ferro Titanium, 25%
Chromium Manganese, 30-70%
Manganese Titanium, 30-35% Titanium
Chromium Copper, 10%
Manganese Boron, 30-35% Boron
Ferro Chromium, 75% Chromium
Cobalt Copper, 10% Cobalt
Cobalt, 97%

GOLDSCHMIDT-THERMIT COMPANY

WILLIAM C. CUNTZ, Gen. Mgr.

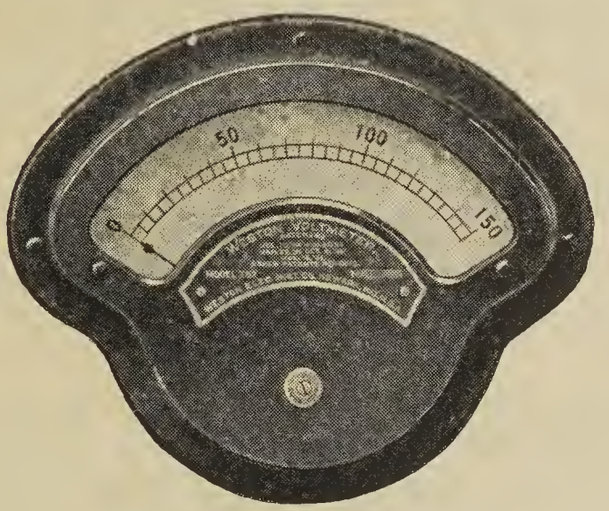
90 WEST STREET, NEW YORK

329-333 Folsom St., San Francisco 103 Richmond St., W., Toronto, Ont.
7300 So. Chicago Ave., Chicago

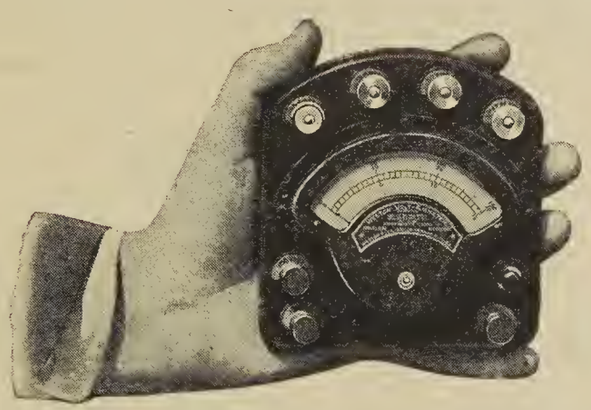
New Weston Miniature Precision Direct Current Instruments

Switchboard and Portable Ammeters, Voltmeters, Milli-voltmeters and Volt-ammeters

MASTERPIECES OF THE INSTRUMENT MAKERS' ART



MODEL 267—SWITCHBOARD INSTRUMENTS



MODEL 280—PORTABLE INSTRUMENTS

For their size, these Miniature Instruments have unsually long and, therefore, very legible scales.

The instruments are very dead-beat, extremely quick in action, and sensitive. They possess the same general characteristics as the highest grade Weston Instruments. Indeed, these Miniature Precision Instruments are a typical Weston product. They are also inexpensive.

We are justified in recommending these Weston Miniature Precision Instruments to all who desire good small direct-current measuring instruments, as being in every way suited for the numerous purposes in which lightness combined with compactness is essential or desirable.

We list nearly 300 different styles and ranges, and carry an enormous stock of finished instruments and parts. Orders can be promptly filled, and the instruments can be safely transported by parcel post.

For full information, send for Bulletin No. 8

WESTON ELECTRICAL INSTRUMENT CO.

New York: 114 Liberty St. **Newark, N. J.**

To produce
Pure OXYGEN
and HYDROGEN

There is no method as *economical* and *reliable* as the **I. O. C. System.** For 1 K. W. H. you obtain 3.5 cubic feet of O. and 7 cubic feet of H. per cell, gases being ***100 percent efficient.***

THE I.O.C. SYSTEM

is practically automatic, requires no expert attention, and costs very little for upkeep.

Write for Particulars

International Oxygen Company

GENERAL SALES OFFICE **115 Broadway, NEW YORK**

Works: NEWARK, N. J.

Pittsburgh, Pa., Park Building — Paris, France, 40 Rue Laffitte

---

"R.I.W."
REMEMBER IT'S WATERPROOF

Damp Resisting Paint

For damp-proofing exposed walls; for stain- and damp-proofing limestone, granite, marble, etc.; for resisting the fumes of acids and alkalies in factories, laboratories, etc., and for preserving steel of different types subjected to various corrosive agencies.

Toch's "Red Book" fully describes these remarkable products, and other Toch Specialties. ***FREE.***

TOCH BROTHERS

ESTABLISHED 1848

Inventors and Manufacturers of TECHNICAL AND SCIENTIFIC PAINTS, ENAMELS, CEMENT COLORS, CEMENT PAINTS, ETC.

320 FIFTH AVENUE, NEW YORK

Works: Long Island City, N. Y., and Toronto, Canada.

CLINTON PAUL TOWNSEND
Ex-Examiner of Electrochemistry U. S. Patent Office

JOHN H. BRICKENSTEIN
Ex-Member Board of Examiners in Chief
U. S. Patent Office

Byrnes, Townsend & Brickenstein

PATENT LAWYERS

National Union Building, 918 F St.

Rooms, 56-61 *WASHINGTON, D. C.*

PERIODICAL